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OF
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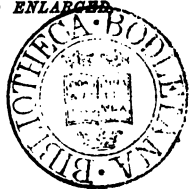
A MANUAL
OF
ELECTRO-METALLURGY :

INCLUDING
THE APPLICATIONS OF THE ART
TO
MANUFACTURING PROCESSES.

BY
JAMES NAPIER, F.R.S.E., F.C.S.

FIFTH EDITION, REVISED AND ENLARGED

With Illustrations.



LONDON:
CHARLES GRIFFIN AND COMPANY,
10 STATIONERS' HALL COURT.
1876.

GLASGOW:
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41 MITCHELL STREET.

PREFACE TO THE FIRST EDITION.

THE author of the following Treatise was engaged for several years in the application of Electro-Metallurgy to the purposes of manufacture. His operations were performed with solutions of all the metals, and upon objects of every size and form. They commenced when the art was young, when its practical applications were speculative, its advantages and disadvantages equally unknown; when difficulties of all kinds, such as beset every new art, had to be met, and considered, and overcome.

The course of his daily proceedings threw him into the way of observations much more extensive and much more diversified than could possibly have occurred to any amateur of the art. Where large operations in an extensive business were concerned, it was necessary to attend to details that some would have considered trifling, and to overcome obstacles that others might have deemed insurmountable. Under the pressure of these circumstances, all means were employed to procure information. Innumerable electrotype processes were repeated as soon as they were published, and original experiments were made in a variety of forms, and frequently on an extensive scale, with a view to the removal of particular difficulties, or to find the means of accomplishing certain desirable ends.

These proceedings and inquiries afforded numerous results, not only useful in the manufacture in which the author was engaged, but interesting to the man of Science. And it is because of their general utility to all persons engaged in the multifarious processes into which the art of Electro-Metallurgy has ramified, that he has been induced to throw them into the form of the following Treatise.

While, however, he can state, that what is collected here is derived from extensive personal experience, he by no means

ventpres to assume that the work is free from deficiencies. He has too frequently had to deplore the effects of his processes, and to point out the desirableness of others of greater certainty and economy.

Neither can the author presume that this work will be a *standard* on the subject to which it relates. Arts and Sciences, like kingdoms and nations, have their several periods of rise, prevalence, and decadence; and nothing can be more unstable than descriptions of an art like Electro-Metallurgy—an art that must fluctuate with the course of experimental discovery, that has rapidly attained a distinguished eminence, and that promises to extend its utility still further over regions now unthought of. The superb specimens of its products, which were displayed to the admiration of the world, at the GREAT EXHIBITION OF THE INDUSTRY OF ALL NATIONS, prove at once the immense importance of Electro-Metallurgy, and how much may yet be expected from one of the most ingenious of those modern applications of Science, which subject the powers of Nature to the use and pleasure of civilised man.

GLASGOW, *May*, 1851.

NOTE TO THE THIRD EDITION.

The rapid sale of the two editions of the *Manual of Electro-Metallurgy* has afforded great gratification to the author, and he has embraced the present opportunity of revisal, to include every approved novelty, so as to bring the work down to the present state of knowledge on this most valuable art.

GLASGOW, *February*, 1857.

PREFACE TO THE FIFTH EDITION.

THE art of Electro-Metallurgy may, in a manner, be said to have passed from the hands of the experimental philosopher into those of the manufacturer; and when at any time the former announces anything new in the art, the latter generally looks upon it from a business standpoint, and asks, "Will it pay?" It is, therefore, not to be wondered at that the manufacturing electro-metallurgist overlooks or forgets many important and interesting phenomena which do not directly affect his manufacturing interests, and that he fails to be sufficiently observant or interested in the theory or science of his art.

It may appear a matter of small consequence to the manufacturing electro-metallurgist whether the electric force which performs his work is composed of two distinct forces—termed a positive and a negative—having, when separated, a strong re-uniting attraction; or one single force, and what are called the negative and positive, simply the possession of more or less of it. I have always held an opinion in favour of the single force, and have, I think, pretty clearly proved that dynamic electricity, at least, is one simple and undecomposable force, by the discovery that when it passes through a fluid in sufficient strength to decompose it, the elements of the fluid are not mutually transferred from one electrode to another, which the compound theory would necessitate, and which is asserted by electricians to take place. I have also shewn that when the electric force passing through any fluid is too weak to decompose it, there is produced a current of the fluid in one direction only, not in opposite directions, as the two and equally-powerful force theory would necessitate. Although upwards of thirty years have elapsed since these facts were made known, subsequent books and lectures on the physical and chemical sciences have

continued to uphold the dogma of two electricities in electrolytic action, causing a mutual transfer of elements from pole to pole. It is no doubt a very pretty theory, only it is not consistent with facts.

I have, in the present edition, gone back to the early days of the art, and produced a number of proofs in vindication of my view. I have also added several things that came under my notice during the active competition which took place between philosophers and manufacturers to gain a step in advance, when the art was new. These have not formed any part of the former editions of this work, and therefore I call the reader's attention to this new matter, because the general form of apparatus now used in the art is not suitable for observing many of the phenomena which were of constant occurrence and often of great annoyance when the art was young.

Notwithstanding the time that has passed since the first edition of this Manual was published, I have not found it necessary to alter, in any essential way, the statements then made respecting the practical operations of the art. No doubt the introduction of the improved electro-magnetic machines have proved of great advantage to the large manufacturer, affecting what might be called the working force, enabling the manufacturer to do as much work in one day, on the same space, as he could have done in a week before. These improved machines are described in this edition.

PARTICK, *2nd Dec., 1875.*

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ELECTRO-METALLURGY.

HISTORY OF THE ART.

IN reviewing the rise and progress of any discovery in the arts and sciences, particularly of one connected with the application of chemistry to manufacturing purposes, there are two circumstances which almost invariably demand especial notice. The FIRST is, that the discovery of the application has been the result of accidental observation—a suggestion eliminated during investigations undertaken for other purposes—rather than the result of a direct endeavour to make the discovery. The SECOND is, that after the discovery has been made known, it is found that many previously published experiments exhibited results which bore more or less directly upon the subsequent discovery, and which are consequently sometimes cited to detract from the merit of the discoverer, and the originality and value of his discovery. The following historical sketch will shew that these observations directly apply to the discovery of the art of Electro-Metallurgy :—

VOLTA'S DISCOVERY.—At the beginning of the year 1800, Professor Volta invented the apparatus which has been named after him, the *Voltaic Pile*. As originally constructed by Volta, it consisted of an equal number of round pieces of zinc, silver, and pasteboard—the zinc and silver pieces being each about the size of a penny, and those of pasteboard a little smaller; the pasteboard pieces were soaked in a solution of common salt, and then with the metals were piled in the following manner :—zinc, silver, pasteboard; zinc, silver, pasteboard; and so on, in the same order, till all the pieces, amounting to upwards of a hundred, were piled upon each other, the uppermost plate being of silver, and, as already stated, the undermost of zinc; these exterior

DECOMPOSITION BY THE BATTERY, AND ITS APPLICATION.—Cruikshanks attached a silver wire to each terminal of his battery, and the other ends of these wires he placed in a glass tube. When this tube was filled with a solution of acetate of lead, and the electric current was allowed to pass through it for some time, metallic lead was found deposited upon the wire attached to the zinc terminal of the battery. Solutions of sulphate of copper, nitrate of silver, and several other salts were tried with similar results. The metals, as Cruikshanks expressed it, were "*revived*," and that so completely as to suggest to him the application of the battery to the analysis of minerals. While Cruikshanks, Nicholson, and several other gentlemen in this country were making investigations and applications of voltaic electricity, Brugnatelli, Fourcroy, Vauquelin, and Thénard, upon the Continent, were making similar investigations, and obtaining similar results.*

DEPOSITION OF METALS UPON OTHERS.—Brugnatelli, in his *Annals of Chemistry*, gives a long list of experiments on the decomposition of salts by the pile. He observed the transfer of the elements of a decomposed compound from one pole to another; that silver, when deposited upon platinum, preserved all its metallic brightness; and that when copper or zinc were used in connection with the silver terminal, or positive pole, of the pile for decomposing salts, these metals were dissolved, and deposited upon the negative pole. The researches of Fourcroy, Vauquelin, and Thénard gave the same results.

GILDING.—In 1805, Brugnatelli, in a letter to Van Mons, mentions, among other scientific facts, that "he had gilt in a complete manner two large silver medals, by bringing them, by means of a steel wire, into communication with the negative pole of a voltaic pile, and keeping them one after the other immersed in ammoniuret of gold newly made and well saturated."†

EARLY OPINIONS CONCERNING ELECTRO-DECOMPOSITION.—The above few instances are selected from a host of a similar kind upon electro-decomposition, to shew that the fact of the deposition of metals by an electric current was familiar to philosophers at this early stage of the history of galvanism; that nevertheless, the phenomenon was

* Wilkinson, *Elements of Galvanism*, vol. II., 1804.

† *Phil. Magazine*, 1805.

never thought of further than as a curious action of electricity when passing through a solution containing metals; and that although these effects were produced again and again, it was only to prove and enforce certain speculative views respecting the electric fluid. As for example, Brugnatelli had formed an idea that the electric fluid had some relations to an acid which he called the *electric acid*, and he therefore viewed the decomposition of solutions, and the obtaining of the metal, which he termed an *electrate*, as the result of the combination of this electric acid with the metal of the solution. In one of his memoirs upon this subject, he says—"Gold and platinum are not sensibly altered by the electric matter which passes through them, though it often happens that the electric current deposits on gold a stratum of zinc, copper, mercury, or silver, according to whichever of these metallic bodies it traverses."* In the same paper it is several times stated that gold and platina do not seem sensibly affected by the *electric acid*. And when he communicated the above experiment of gilding the two medals, his object was to shew that he had now found that the electric acid had also the power of acting upon gold; and the publication of these results and observations excited no other idea in the minds of philosophers of that period than that they were mere scientific curiosities. The editor of the *Philosophical Magazine* appended the following note to the extract already quoted:—"The result here detailed reminds me of one somewhat similar, which took place during some experiments performed some years ago in the Askesian Rooms. Some gold leaf was put loose upon a new piece of copper coin, which was then brought into the circuit of the pile. A part of the gold was inflamed, and other portions adhered to the surface of the copper as completely as if they had been attached by any common gilding process."†

HOW THESE RESULTS AFFECT THE DISCOVERY.—We have been particular in thus noticing the observations of the first pioneers in electro-chemistry, because these and similar facts of later date have been brought prominently forward by writers upon electro-metallurgy, with the apparent intention to detract from the merit due to the discoverers of the new art, basing their argument on the ground that the *principle* upon which the discovery is founded is not new. "Electro-metallurgy," says Mr. Smee, "may be said to have its origin in the discovery of the constant battery by Professor Daniell, for in that instrument the copper

* Brugnatelli, *Annals of Chemistry*, vol. xviii., and Wilkinson, vol. ii.

† *Phil. Magazine*, 1805.

is continually reduced upon the negative plate." And again, when speaking of Daniell's battery, he says—"Mr. M. De la Rue experimented on its properties, and found the copper plate also covered with a coating of metallic copper, which is continually being deposited; and so perfect is the sheet of copper thus formed, that being stripped off, it has the counterparts of every scratch of the plate on which it is deposited." *

Doubtless these experiments border very closely upon the discovery; but yet they have no more claim to serve as dates to its origin than those we have been referring to. But if it be necessary that an originating experiment must have a resemblance to that which it suggests—such as Daniell's battery, and the single cell of electro-metallurgy—why omit to refer to Dr. Wollaston's earlier experiments of 1801? He says—"If a piece of silver, in connection with a more positive metal, be put into a solution of copper, the silver is coated over with the copper, which coating will stand the operation of burnishing."† But in our opinion none of these results originated electro-metallurgy: the discovery of that art, although it is an application of such results as we have described, was as original on the part of the discoverers, and as unconnected with these results at the time it was made, as it would have been had the earlier observations never been published. The discovery seems to have been deduced from results which the discoverers had obtained in their own experiments, not even while searching for such a discovery, but during investigations instituted for other purposes.

USE OF OBSERVED FACTS.—It must not be supposed that we depreciate the value of the published facts upon the decomposition of salts, nor that we overlook their relation to the discovery which followed; for the multiplication of facts, and the improvement of instruments for experimenting, enlarge our knowledge of the principles to be investigated or applied; they facilitate inquiry, and increase the number of observers. What we mean is, that the discovery of the art of electro-metallurgy is not the discovery of the fact that a current of electricity passing through a solution of a compound decomposes that compound, and that if the compound be a salt of a metal, the metallic element will be deposited upon one of the electrodes; but it is the idea of applying this fact to the arts and manufactures of the country, and the carrying out this idea to a practical issue. None of the published experiments upon the decomposition of salts by an electric current ever suggested their application

* Smee, *Elements of Electro-Metallurgy*, 2nd Edition, 1843.

† *Philosophical Transactions*, 1801.

to the arts. Cruikshanks did suggest its application to the assaying of metallic ores—a suggestion repeated by others many years after, and adopted for a time by several chemists; and Dr. Wollaston's hint that copper deposited upon silver could stand the operation of burnishing was not taken advantage of, and cannot be put forth as suggesting electro-metallurgy. The circumstances connected with the discovery of the art of electro-metallurgy—of the application of the decomposing force of an electro current passing through a solution, will illustrate these observations.

SPENCER'S FIRST EXPERIMENTS.—Mr. Thomas Spencer, of Liverpool, states that, in 1837, while experimenting with a modification of a Daniell's battery, he used a penny piece instead of a plain piece of copper, as a pole. Copper was deposited from the solution upon it, and on removing the wire which attached the penny to the zinc plate he also pulled off a portion of the deposited copper, which he found to be an exact counterpart or mould of a part of the head and letters of the coin *as smooth and sharp as the original*. But this did not suggest to him any useful application, and was no more than Daniell and others had observed, and not until some time after he dropped, accidentally, a little varnish upon a slip of copper which he was about to use in the same way as he had used the penny piece. On finding that no deposit of copper took place on the parts where the varnish had dropped, he then conceived the idea of applying this principle to the arts, by coating a piece of copper with varnish or wax, and cutting a design through the wax or varnish, leaving the copper bare, and then depositing upon these parts, so that upon removing the varnish the design would be left in relief. We thus see that Mr. Spencer's first idea of the application of depositing a metal from a solution to the arts was very limited—an application that has never been very extensively carried into practice, although several patents have been taken out for the purpose of forming by this means printing blocks both for paper and calico.

JACOBI'S EXPERIMENTS.—While Mr. Spencer was following up these ideas, the following paragraph appeared in the *Athenæum* for 4th May, 1839 :—

“*Galvanic Engraving in Relief*.—While M. Daguerre and Mr. Fox Talbot have been dipping their pencils in the solar spectrum, and astonishing us with their inventions, it appears that Professor Jacobi, at St. Petersburg, has also made a discovery which promises to be of

little less importance to the arts. He has found a method—if we understand our informant rightly—of converting any line, however fine, engraved on copper, into a relief, by galvanic process. The Emperor of Russia has placed at the professor's disposal funds to enable him to perfect his discovery."

In consequence of this announcement, Mr. Spencer, on the 8th of May, 1839, gave notice to the Liverpool Polytechnic Institution, that he should make a communication to them of his process for effecting results similar to those of Professor Jacobi. But Mr. Spencer appears to have changed his intention of reading it to the above institution, in order to have it read at the meeting of the British Association, which was to take place a short time after.

JORDAN'S EXPERIMENTS.—Meanwhile the announcement of the *Athenæum* was quoted in the *London Mechanics' Magazine* for May 11th, 1839, which brought forth a letter from Mr. C. J. Jordan, a book printer, dated 22nd May, 1839, and published on the 8th June of the same year in the *London Mechanics' Magazine*. In this letter Mr. Jordan describes his experiments upon the same subject, detailing the method of procuring electrotypes, and offering hints for their application which have since been acted upon with considerable success. The following is a copy of Mr. Jordan's letter, which was, no doubt, the first published description of the art in this country:—

Engraving by Galvanism.

"Sir,—Observing in the last page of a recent number of your magazine a notice extracted from the *Athenæum*, relative to a discovery of Professor Jacobi, its perusal occasioned the recollection of some experiments performed about the commencement of last summer, with the view of obtaining impressions from engraved copper plates, by the aid of galvanism, which led me to infer some analogy in principle with those of the Russian professor, and may probably give me the right to claim priority in its discovery and application. These experiments were abandoned from the want of that most important element in pursuits of this nature—time, the writer's share of the said element being occupied in a manner more imperative than pleasing. I regret, however, not having made it the subject of an earlier communication, as this would have placed my pretensions beyond doubt; but inasmuch as the notice alluded to is given from memory, and is undescriptive, while I may be enabled to exhibit the *modus operandi*, my assertion may be at least partially substantiated.

"It is well known to experimentalists on the chemical action of voltaic electricity, that solutions of several metallic salts are decomposed by its agency, and the metal procured in a free state. Such results are very conspicuous with copper salts, which metal may be obtained from its sulphate (blue vitriol), by simply immersing the poles of a galvanic battery in its solution, the positive wire becoming gradually coated with copper. This phenomenon of metallic reduction is an essential feature in the action of sustaining batteries, the effect, in this case, taking place on more extensive surfaces. But the form of voltaic apparatus which exhibits this result in the most interesting manner, and relates more immediately to the subject of the present communication, may be thus described:—It consists of a glass tube, closed at one extremity with a plug of plaster of Paris, and nearly filled with a solution of sulphate of copper; this tube and its contents are immersed in a solution of common salt. A plate of copper is placed in the first solution, and is connected, by means of a wire and solder, with a zinc plate which dips into the latter. A slow electric action is thus established through the pores of the plaster, which it is not necessary to mention here—the result of which is the precipitation of minutely crystallised copper on the plate of that metal, in a state of greater or less malleability according to the slowness or rapidity with which it is deposited. In some experiments of this nature, on removing the copper thus formed, I remarked that the surface in contact with the plate equalled the latter in smoothness and polish, and mentioned this fact to some individuals of my acquaintance. It occurred to me, therefore, that if the surface of the plate was engraved, an impression might be obtained. This was found to be the case; for, on detaching the precipitated metal, the most delicate and superficial markings, from the fine particles of powder used in polishing to the deeper touches of a needle or a graver, exhibited their correspondent impressions in relief with great fidelity. It is, therefore, evident that this principle will admit of improvement, and that casts and moulds may be obtained from any form of copper.

"This rendered it probable that impressions may be obtained from those other metals having an electro-negative relation to the zinc plate of the battery. With this view, a common printing type was substituted for the copper plate, and treated in the same manner.

This also was successful; the reduced copper coated that portion of the type immersed in the solution. This, when removed, was found to be a perfect matrix, and might be employed for the purpose of casting where time is not an object.

"It appears, therefore, that this discovery may be turned to some

practical account. It may be taken advantage of in procuring casts from various metals, as above alluded to; for instance, a copper die may be formed from a cast of a coin or medal in silver, type metal, or lead, &c., which may be employed in striking impressions in soft metals. Casts may probably be obtained from a plaster surface surrounding a plate of copper; tubes or any small vessels may also be made by precipitating the metal around a wire, or any kind of surface, to form the interior, which may be removed mechanically by the aid of an acid solvent or by heat.

“C. J. JORDAN.

“To the Editor of the London Mechanics' Magazine.”

Clear and perspicuous as this letter is, it did not attract the slightest notice. And a few weeks after, we find that its existence was forgotten even by the editor of the magazine in which it appeared.

SPENCER'S FIRST PRINTED PAPER UPON ELECTROTYPE.—Mr. Spencer's communication referred to above, was, in consequence of some misunderstanding, not read at the meeting of the British Association, but it was immediately afterwards read before the Polytechnic Institution of Liverpool, at their meeting on the 13th September, 1839, which was upwards of three months after the publication of Mr. Jordan's letter in the *London Mechanics' Magazine*. Mr. Spencer's paper was accompanied with specimens both of electrotypes and of printing from electrotypes. The publication of this paper acted like an electric shock upon society, and men both of science and art became active competitors in this new field of application; the one class anxious to bear away the honours arising from some important improvement; the other, the profits which might follow some novel application of the process to their own or some other branch of manufacture. Indeed, thousands of all classes and ages, who had never previously given science a passing thought, became fascinated with the new art, and—the process being simple and easy to perform—the amateurs soon became excellent electrotypists. With these combined efforts, it need not be wondered at that in a very short time improvements of great scientific interest were pointed out, and applications of the greatest importance to the arts and manufactures of this country were introduced. In consequence, some of our old and standard manufactures, as we shall subsequently have occasion to notice at some length, have been completely revolutionised.

HISTORICAL ANOMALY.—During a period of nearly five years—while the country was passing through an electrotyping mania—Mr. Spencer held the undivided honour of being the first to apply the deposition of metals to practical purposes in this country; but early in 1844, Mr. Henry Dircks, in a letter to the *London Mechanics' Magazine*, revived Mr. Jordan's letter, and told us that he was aware of its existence from the time of its first publication. We cannot eulogise either the policy, or the love of scientific truth, which induced Mr. Dircks to remain silent so long, and see the claims of Mr. Jordan set aside by one whom he considered to be a mere pretender to the merit of the discovery. Nor after a careful and impartial examination of all the details published on the subject, can we agree to his condemnation of Mr. Spencer's prior claims; as he, Mr. Spencer, upon the 8th of May, as already noticed, stated to a public meeting of the Polytechnic Society of Liverpool, that he had made a similar discovery previous to any knowledge of either what Jordan or Jacobi had done, and which was a publication as much as if printed in the *Times* or *Athenæum*, and especially when followed by a detailed description of the discovery.

It is to be regretted that Mr. Jordan's diffidence, which in this case was far from being commendable, prevented his setting the public right upon this important matter. As a consequence, he must now be content with a much smaller share of the honour of the discovery than he might have enjoyed.

On reviewing the circumstances of this discovery, it strikes us as being a remarkable instance of the unity of intellectual perception in reference to the general principles of Nature and their applications; for we believe that Professor Jacobi, Mr. Spencer, and Mr. Jordan viewed the subject of electro-depositions in the same light, and about the same time; and each, according to their several abilities, presented to the public the same discovery, independent of the other, excepting the announcement made by one having hastened the publication of the observations of the others.

It is remarkable that the applications referred to by all the three discoverers are nearly of the same character, and connected with printing. None of the three seems to have seen the more direct application of the deposition of one metal upon another as a coating, either as a protection against oxidation, as covering iron with copper, tin, or zinc, or for coating cheap and inferior metals with the precious and expensive metals, such as plating and gilding. That application was reserved for those who understood these arts and their requirements.

The following is Mr. Spencer's original paper on electro-metallurgy, which we give at length, trusting that its importance in connection with the history of the art, and the lucid description of its practice, will serve as a sufficient apology for not abridging it:—

“ON WORKING IN METAL BY VOLTAIC ELECTRICITY, REPRINTED FROM THE PAPER PUBLISHED BY THE LIVERPOOL POLYTECHNIC SOCIETY, AND READ AT THE MEETING OF SEPTEMBER THE 12TH, 1839, NOTICE BEING GIVEN MAY THE 8TH—HENRY BOOTH, ESQ., PRESIDENT, IN THE CHAIR.

“In the paper that I have the honour to lay before the Society, I do not profess to have brought forward a perfect invention. My only object is to point out a means by which, I hope, practical men may be enabled to apply a great and universal principle of Nature to the useful and ornamental purposes of life. In this I may be considered sanguine—an error, I am aware, too often fallen into by those who, like myself, imagine they have discovered a useful application of an important principle; but however this may fall out, I shall lay an account of its results, with specimens, successful and unsuccessful, before the members and the public,—previously stating, however, that all my first experiments were made on a small scale—a method of procedure attended with many advantages to the experimentalist himself, but having its disadvantage when laid before the public. In this first respect, perhaps, the chemical experimenter has an advantage over the mechanical one, as the success of his experiment, when tried on a small scale, doubly guarantees it if conducted on a still larger scale; with mechanical results I believe in most instances it is the reverse. But when the chemist produces his microscopic proofs, the public are generally slow to believe that such minute appearances should warrant him in coming to any general conclusion.

“In the latter part of September, 1837, I was induced to make some electro-chemical experiments, with single pairs of plates, consisting of small pieces of zinc and equal-sized pieces of copper, connected together with wires of the latter metal. It was intended that the action should be slow: the fluids in which the metallic electrodes were immersed were in consequence separated by thin discs of plaster of Paris. In one cell thus formed was placed sulphate of copper in solution,—in the other, a weak solution of common salt. I need scarcely add that the copper electrode was placed in the cupreous solution, the other being in that of the salt. I mention these experiments briefly,—not because they are directly connected with what I

shall have to lay before the Society, but because, by a portion of their results, I was induced to come to the conclusions I have done in the following paper. I was desirous that no action should take place on the wires by which the electrodes were held together; and to attain this object I varnished them with sealing-wax varnish; but in one instance I dropt a portion on the copper electrode that was attached. I thought nothing of this circumstance at the moment, but put the experiment in action.

"This operation was conducted in a glass vessel; I had consequently an opportunity of occasionally examining its progress from the exterior. After the lapse of a few days, metallic crystals had covered the copper electrode,—*with the exception of that portion* which had been spotted with the drops of varnish. I at once saw that I had it in my power to guide the metallic deposition in any shape or form I chose, by a corresponding application of varnish or other non-metallic substance.

"I had been aware of what every one who uses a sustaining galvanic battery with sulphate of copper in solution must know, that the copper plates acquire a coating of copper from the action of the battery; but I had never thought of applying it to a useful purpose, except to multiply the plates of a species of battery, which I did in 1836. My present attempt was with a piece of thin copper plate, having about four inches of superficies, with an equal-sized piece of zinc, connected as before by a piece of copper wire. I gave the copper a coating of soft cement, consisting of bees-wax, resin, and a red earth. It was compounded in the manner recommended by Dr. Faraday, in his work on *Chemical Manipulation*, but with a larger proportion of wax. The plate received its coating while hot. When it was cold, I scratched the initials of my name rudely on the plate, taking special care that the cement was quite removed from the scratches, that the copper might be thoroughly exposed. This was put in action in a cylindrical glass vessel, about half filled with a saturated solution of sulphate of copper. I then took a common gas glass, similar to that used to envelop an argand burner, and filled one end of it with plaster of Paris, to the depth of three-quarters of an inch. Into this I put water, adding a few crystals of sulphate of soda to excite action, the plaster of Paris acting as a partition to separate the fluids, but at the same time being sufficiently porous to allow the electro-chemical action to permeate its substance.

"I now bent the wire in such a manner that the zinc end of the arrangement should be in the saline solution, while the copper end,

when in its place, should be in the cupreous solution. The gas glass, with the wire, was then placed in the vessel containing the sulphate of copper.

"It was then suffered to remain at rest, when in a few hours I perceived that action had commenced, and that the portion of the copper rendered bare by the scratches had become gradually coated with pure bright deposited metal, whilst all the surrounding portions were not at all acted on. I now saw my former observations realised; but whether the deposition so formed would retain its hold on the plate, and whether it would be of sufficient solidity or strength to bear the working if applied to a useful purpose, became questions which I now determined to solve by experiment. It also became a question—should I be successful in these two points—whether I should be able to produce lines sufficiently in relief to print from. This latter appeared to depend entirely on the nature of the cement or etching-ground I might use.

"This I endeavoured to solve at once; and, I may state, it appeared at the time to be the main difficulty, as my impression then was, that little less than one-eighth of an inch of relief would be requisite to print from.

"I now procured a piece of copper, and gave it a coating of a modification of the cement I have already mentioned, and having covered it to about one-eighth of an inch in thickness, I took a steel point and endeavoured to draw lines in the form of network, that should entirely penetrate the cement, and leave the surface of the copper exposed. But in this I experienced much difficulty from the thickness I deemed it necessary to use, more especially when I came to draw the cross lines of the network. The cement being soft, the lines were pushed, as it were, into each other, and when it was made of harder texture, the intervening squares of the network chipped off the surface of the metallic plate. However, those that remained perfect I put in action as before.

"In the progress of this experiment I discovered that the solidity of the metallic deposition depended entirely on the weakness or intensity of the electro-chemical action, which I knew I had in my power to regulate at pleasure, by the thickness of the intervening wall of plaster of Paris, and by the coarseness or fineness of the material. I made three similar experiments, altering the texture and thickness of the plaster each time, by which I ascertained that if the partitions were *thin* and *coarse*, the metallic depositions proceeded with great *rapidity*, but the crystals were friable and easily separated; on the other hand, if I made them thicker, and of a little finer material, the action was *slower*,

but the metallic deposition was as solid and ductile as copper formed by the usual methods,—indeed, when the action was exceedingly slow. I have had a metallic deposition apparently much harder than common sheet copper, but more brittle.

“There was one most important and, to me, discouraging circumstance attending these experiments, which was, that when I heated the plates to get off the covering of cement, the meshes of copper network occasionally *came off with it*. I at one time imagined this difficulty inseparable, as it appeared that I had cleared the cement entirely from the surface of the copper that I meant to have exposed; and I concluded that there must be difference in the molecular arrangement of copper prepared by heat and that prepared by voltaic action, which prevented their chemical combination. However, I determined, should this prove so, to turn it to account in another manner, which I shall relate in the second portion of the paper.

“I now occupied myself for a considerable period in making experiments on this latter section of the subject.

“In one of them I found, on examination, that a portion of the copper deposition, which I had been forming on the surface of a coin, adhered so strongly that I was quite unable to get it off,—indeed, a chemical combination had apparently taken place. This was only on one or two spots on the prominent parts of the coin. I immediately recollected that, on the day I put the experiment in action, I had been using nitric acid for another purpose on the table I was operating on, and that in all probability the coin might have been laid down where a few drops of the acid had accidentally fallen. Bearing this in view, I took a piece of copper, coated it with cement, made a few scratches on its surface until the copper appeared, and immersed it for a short time in dilute nitric acid, until I perceived, by an elimination of nitrous gas, that the exposed portions were acted upon sufficiently to be slightly corroded. I washed the copper in water, and put it in action as before described. In forty-eight hours I examined it, and found the lines were entirely filled with copper. I applied heat, and then spirits of turpentine, to get off the cement, and, to my satisfaction, I found that the voltaic copper had completely combined itself with the sheet on which it was deposited.

“I then gave a plate a coating of cement to a considerable thickness, and sent it to an engraver; but when it was returned I found the lines were cleared out so as to be wedge-shaped, or somewhat in the form of a ∇ , leaving a hair-line of the copper exposed at the bottom, and a broad space near the surface; and where the turn of the letters took

place, the top edges of the lines were galled and rendered rugged by the action of the graver. This, of course, was an important objection, which I have since been able to remedy in some degree by an alteration in the shape of the graver, which should be made of a shape more resembling a narrow parallelogram than those in common use: some engravers have many of their tools so made. I did not put this plate in action, as I saw that the lines, when in relief, would have been broad at the top and narrow at the bottom. I took another plate, gave it a coating of the wax, and had it written on with a mere point. I deposited copper on the lines, and afterwards had it printed from.*

"I now considered part of the difficulties removed: the principal one yet remaining was to find a cement or etching-ground, the texture of which should be capable of being cut to the required depth, without raising what is technically termed a *burr*, and at the same time of sufficient toughness to adhere to the plate when reduced to a small isolated point, which would necessarily occur in the operation which wood-engravers term cross-hatching.

"I have since learned, from practical engravers, that much less relief is necessary to print from than I had deemed indispensable, and that, on becoming more familiar with the cutting of the wax-cement, they would be enabled to engrave in it with great facility and precision.

"I tried a number of experiments with different combinations of wax, resins, varnishes, earths, and metallic oxides, all with more or less success. One combination that exceeded all others in its texture was principally composed of bees'-wax, resin, and white lead. This had nearly every requisite, so that I was enabled to polish the surface of the plate with it until it was nearly as smooth as a plate of glass. With this compound I had two plates, five inches by seven, coated over, and portions of maps cut on the cement, which I had intended should have been printed off. I applied the same process to these as to the others, immersing them into dilute nitric acid before putting them in action—indeed, I suffered them to remain about ten minutes in the solution. I then put them into the voltaic arrangement. The action proceeded slowly and perfectly for a few days, when I removed them. I applied heat, as usual, to remove the cement, but *all* came away, as in a former instance—the voltaic copper peeling off the plate with the greatest facility. I was much puzzled at this unexpected result; but, on cleaning the plate, I discovered a delicate trace of *lead*, exactly corresponding to the lines drawn on the cement previous to the immersion in the dilute acid. The cause of this failure was at once obvious: the carbonate of

* This plate was shewn to friends, and also specimens of printing from it, in 1838.

lead I had used to compound the etching-ground had been decomposed by the dilute nitric acid, and the metallic lead thus reduced had deposited itself on the exposed portions of the copper plates, preventing the voltaic copper from chemically combining with the sheet copper. I was now with regret obliged to give up this compound and to adopt another, consisting of bees'-wax, common resin, and a small portion of plaster of Paris. This seems to answer the purpose tolerably, though I have no doubt, by an extended practice, a better may still be obtained by a person practically acquainted with the etching-grounds in use among engravers.

"I now proceed to the second, and I believe the most satisfactory portion of the subject. Although I have placed these experiments last, some of them were made at the same time with the others already described, and some of them before; but to render the subject more intelligible, I have placed them thus.

"The members of the Society will recollect that, on the first evening it met, I read a paper on the 'Production of Metallic Veins in the Crust of the Earth,' and that among other specimens of cupreous crystallisation which I produced on that occasion, I exhibited two coins—one wholly covered with metallic crystals, the other on one side only. It was used under the following circumstances:—When about to make the experiment, I had not a slip of copper at hand to form the negative end of my arrangement, and, as a good substitute, I took a penny and fastened it to one end of the wire, and put it, in connection with a piece of zinc, in the apparatus already described.

"Voltaic action took place, and the copper coin became covered with a deposition of copper in a crystalline form. But when about to make another experiment, and being desirous of using the piece of wire used in the first instance, I pulled it off the coin to which it was attached. In doing this, a piece of the deposited copper came off with it; on examining the under portion of which, I found it contained an exact mould of a part of the head and letters of the coin, as smooth and sharp in every respect as the original on which it was deposited. I was much struck with this at the time; but, on examination, the deposited metal was very brittle. This, and the fact that it would require a metallic nucleus to aggregate on, made me apprehensive that its future usefulness would be materially abridged; but it was reserved for future experiment, and in consequence laid aside for a time, until my attention was recalled to the subject in a subsequent experiment, already detailed, by the drops of varnish on a slip of copper. Finding in that instance that the deposit would take the direction of any non-conducting material, and

be, as it were, guided by it, I was induced to give the previous branch of the subject a second trial, because I had, in the first instance, supposed that the deposition would only take place continuously, and not on isolated specks of a metallic surface, as I now found it would ; but the principal inducement to investigate the subject was the fact of finding that the deposited copper had much more tenacity than I at first imagined.

"Being aware of the apparent natural law which limits metallic deposition by voltaic electricity, excepting in the presence of a metallic body, I perceived that the uses of the process would in consequence be extremely limited, except in the multiplication of already engraved plates, as, whatever ornament it might produce, it would only be done by adhering to the condition of a metallic mould.

"I accordingly determined to make an experiment on a very prominent copper medal. It was placed in a voltaic circuit, as already described, and deposited a surface of copper on one of its sides, to about the thickness of a shilling. I then proceeded to get the deposition off. In this I experienced some difficulty, but ultimately succeeded. On examination with a lens, every line was as perfect as the coin from which it was taken. I was then induced to use the same piece again, and let it remain a much longer time in action, that I might have a thicker and more substantial mould, in order to test fairly the strength of the metal. It was accordingly put again in action, and let remain until it had acquired a much thicker coating of the metallic deposition ; but on attempting to remove it from the medal I found I was unable. It had apparently completely adhered to it.

"I had often practised with some degree of success a method of preventing the oxidation of polished steel, by slightly heating it until it would melt fine bees'-wax ; it was then wiped apparently completely off, but the pores or surface of the metal became impregnated with the wax.

"I thought of this method, and applied it to a copper coin.

"I first heated it, applied wax, and then wiped it so completely off, that the sharpness of the coin was not at all interfered with. I proceeded as before, and deposited a thick coating of copper on its surface. Being desirous to take it off, I applied the heat of a spirit-lamp to the back, when a sharp crackling noise took place, and I had the satisfaction of perceiving that the coin was completely loosened. In short, I had a most complete and perfect copper mould of one side of a halfpenny.

"I have since taken some impressions from the mould thus taken, and by adopting the above method with the wax, they are separated with the greatest ease.

"By this experiment it would appear that the wax impregnates the surface of the metal to an inconsiderable depth, and prevents a chemical adhesion from taking place on the two surfaces; and I can only account for the crackling noise on separation, by supposing it probable that the molecular arrangement of the voltaic metal is different from that subjected to percussion, and this difference causes an unequal degree of expansibility on the application of heat.

"I became now of opinion that this latter method might be applied to engraving much better than the method described in the first portion of this paper. Having found in a former experiment that copper in a voltaic circuit deposited itself on lead with as much rapidity as on copper, I took a silver coin and put it between two pieces of clean sheet-lead, and placed them under a common screw-press. From the softness of the lead, I had a complete and sharp mould of both sides of the coin, without sustaining injury. I then took a piece of copper wire, soldered the lead to one end and a piece of zinc to the other, and put them into the voltaic arrangement I have already described. I did *not* in this instance *wax* the mould, as I felt assured that the deposited copper would easily separate from the lead by the application of heat, from the different expansibility of the two metals.

"In this result I was not disappointed. When the heat of a spirit-lamp was applied for a few seconds to the lead, the copper impression came easily off. So complete do I think this latter portion of the subject, that I have no hesitation in asserting that *fac-similes* of any coin or medal, no matter of what size, may be readily taken, and as sharp as the original. To test further the capabilities of this method, I took a piece of lead plate, and stamped some letters on its surface to a depth sufficient to print from when in relief. I deposited the copper on it, and found it came easily off, the letters being in relief.

"Finding from this experiment that the extreme softness of lead allowed it to be impressed on by type metal, I caused a small portion of ornamental letterpress to be set up in type, and placing it on a planed piece of sheet-lead, it was subjected to the action of a screw-press.

"After considerable pressure, it was found that a perfectly sharp mould of the whole had been obtained in the lead. A wire was now soldered to it, and it was placed in an apparatus similar in principle, but larger than the one already described. At the end of eight days from this time, copper was deposited to one-eighth of an inch in thickness; it was then removed from the apparatus, and the rough edges of the deposited copper being filed off, it was subjected to heat, when the

two metals began to loosen. The separation was completed by inserting a piece of wedge-shaped wood between them.

"I had now the satisfaction of perceiving that I had by these means obtained a most perfect specimen of stereotyping in copper, which had only to be mounted on a wooden block to be ready to print from.

"From the successful issue of this experiment, which was mainly due to the susceptibility of the lead, I was induced to attempt to copy a wood engraving by a similar method, provided the wood would bear the requisite pressure. Knowing that wood engravings are executed on the *end* of the block, I had better hopes of succeeding, the wood being less likely to sustain injury.

"I accordingly procured a small wood block, and placed its engraved surface in contact with a piece of sheet lead made very clean, and subjected it to pressure as in the former instance. I had now, as before, the gratification of perceiving that a perfect mould of the little block had been obtained, and no injury done to the original. Several wood engravings and copperplates were subjected to similar treatment, and are now in process of being deposited on in the apparatus before me.

"I now come to the third and concluding portion of the experiments on this subject. The object being to deposit a metallic surface on a model of clay, wood, or other *non-metallic* body, as otherwise I imagined the application of this principle would be extremely limited. Many experiments were made to attain this result, which I shall not detail, but content myself with describing those which were ultimately most successful.

"I procured two models of an ornament,—one made of clay, and the other of plaster of Paris—soaked them for some time in linseed-oil, took them out, and suffered them to dry, first getting the oil clean off the surface. When dry, I gave them a thin coat of mastic varnish. When the varnish was nearly dry, *but not thoroughly so*, I sprinkled some bronze powder on that portion I wished to make a mould of. This powder is principally composed of mercury and sulphur, or it may be chemically termed a sulphuret of mercury. There is a sort that acts much better, in which is a portion of gold. I had, however, a complete metalliferous coating on the surface of the model, by which I was enabled to deposit a surface of copper on it by the voltaic method I have already described. I have also gilt the surface of a clay model with gold leaf, and have been successful in depositing copper on its surface. There is likewise another, and, as I trust it will prove, a simpler method of attaining this object; but as I have not yet sufficiently tested it by experiment, I shall take another opportunity of describing it."

[At the close of the paper, several specimens of coins, medals, and copper plates, some of them in the act of formation by the voltaic process, were exhibited by Mr. Spencer to the Society.]

PLUMBAGO AS A COATING.—Shortly after Mr. Spencer's paper was published, several important improvements were introduced, one or two of which we will refer to here, and will give the others when detailing the processes to which the improvements were applied. The first was the use of plumbago or blacklead, to give the surface of non-metallic bodies a conducting property. This was the discovery of the late Mr. Robert Murray, a gentleman of high attainments and unassuming manners, who communicated the process to the members of the Royal Institution orally. The Society of Arts afterwards awarded to Mr. Murray a silver medal, as an expression of their sense of the value of the discovery. Seldom was reward more deserving, or a discovery more important to the purposes to which it was to be applied, for this application at once freed electro-metallurgy from every bond: it was no longer necessary to use either metallic moulds, or moulds having metal reduced upon their surfaces by chemical means—which, according to the processes then known, was both tedious and uncertain, and only applicable to certain substances. Plumbago possessed all the requisite properties: it was convenient, plentiful, and cheap, easily applied, and equally effective for every substance on which the electrotypist desired to obtain a deposit, or which he could wish to cover with metal, either for useful or ornamental purposes.

SEPARATE BATTERY.—The second improvement is one that must have followed the original discovery very soon, namely, the application of a *separate battery* for the purposes of deposition. Although those instances of deposition of metals which have been referred to in the early history of galvanism were effected by means of separate batteries,—namely, by placing the ends of the wires attached to the terminals of the battery in the solution to be decomposed, still the discovery under consideration was made by means of what is termed the *single cell*, or modification of Daniell's battery. It consisted in simply attaching by a wire the article upon which a deposition was to be made to a piece of zinc, and immersing the zinc in diluted acid, and the other article in a solution of the metal to be deposited; the two liquids being separated by a porous partition, or diaphragm, such as moist bladder or unglazed porcelain. In this case the whole electricity was expended within the cell, to

deposit the metal within or upon the mould. Mr. Mason suggested making the original arrangement, or single cell, the generating cell or battery to a second cell. In this last cell was also a solution of a metal having in it a sheet of similar metal attached to the copper of the first cell, and the mould to be covered was attached to the zinc of the first cell. Fig. 2 is an illustration of Mason's improvement, which consisted in causing a medal, in the act of being deposited, to serve as a battery for the deposition of another medal. O^2 , Outer vessel filled with sulphate of copper; O^1 , another vessel, with P, a porous cell filled with dilute acid, in which is placed Z, a zinc plate, which is connected by a wire with a medal m' in the second vessel charged with sulphate of copper. The medal, m , in the first cell, O^1 is connected by a wire to a piece of copper, C , in the second cell O^2 : the electricity passes from the zinc Z to m , and by the wire to C , then to m' , and by the wire back to the zinc Z .

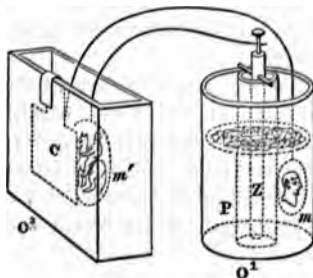


Fig. 2.

This arrangement of battery has not been of much use in the arts, or indeed in the operations of electrotyping: the ostensible object was economy, but it is a very questionable economy, and quite unsuited for manufacturing purposes where batteries are used, at the same time. The suggestion was at once expanded into the using of a separate battery of any convenient construction to the purpose of depositing metals from their solutions in vessels outside of the battery, thus putting into the hands of the manufacturing electro-metallurgist an instrument applicable to all kinds of solutions and metals, which the single cell was not, although for making and copying of medals in copper we consider the single cell process the best.

LAWS OF DEPOSITION.—As might have been expected in the excitement occasioned by the announcement of a new art, every individual experimenter became so engrossed by his own investigations and their results, as to overlook the labours of others, and at last to lay claim to the honour of originating *all* the discoveries they announced; while the truth is, that nearly all the important facts of electro-metallurgy appear to have occurred almost simultaneously to various experimenters. We shall quote one or two instances of these absorbing claims, as it is important to rectify the errors they contain, because no successful

labourer, however humble, in the field of science or art, should be overlooked by his fellow-labourer, whose opportunities for research may be much more favourable.

Extract from SMEE'S "Electro-Metallurgy."

"The laws regulating the reduction of all metals in different states were first given in this work as the result of my own discoveries. By these we can throw down gold, silver, platinum, palladium, copper, iron, and almost all other metals, in three states, namely,—as a black powder, as a crystalline deposit, or as a flexible plate. These laws appear to me at once to raise the isolated facts known as the electrotype into a science, and to add electro-metallurgy as an auxiliary to the noble arts of this country."

That Mr. Smee discovered the laws referred to we have not the slightest doubt: they were published as laws in his book, and they are commonly quoted as Mr. Smee's; nevertheless, he was not the first who discovered them; the same laws were pointed out by Mr. Spencer, in his original paper just quoted, published eighteen months previously to the appearance of Mr. Smee's work, as will be seen from the following extracts:—

Laws given by Smee.

"Law I.—The metals are invariably thrown down as a black powder when the current of electricity is so strong, in relation to the strength of the solution, that hydrogen is evolved from the negative plate of the decomposition cell.

"Law II.—Every metal is thrown down in a crystalline state, when there is no evolution of gas from the negative plate, or no tendency thereto.

"Law III.—Metals are reduced in the reguline state when the quantity of electricity, in relation to the strength of the solution, is

Laws given by Spencer.

"I discovered that the solidity of the metallic deposition depended entirely on the weakness or intensity of the electro-chemical action, which I knew I had in my power to regulate at pleasure, by the thickness of the intervening wall of plaster of Paris, and by the coarseness or fineness of the material. I made three similar experiments, altering the texture and thickness each time, by which I ascertained, that if the partitions were *thin* and *coarse*, the metallic deposition proceeded with *great rapidity*, but the crystals were friable and easily separated; on the other hand, if I made them thicker,

insufficient to cause the production of hydrogen in the negative plate of the decomposition trough, and yet the quantity of electricity very nearly suffices to induce that phenomenon."

and of a little finer material, the action was slower, but the metallic deposition was as solid and ductile as copper formed by the usual methods. Indeed, when the action was exceedingly slow, I have had a metallic deposition much harder than common sheet copper, but more brittle."

The identity of these deductions or laws requires no comment; and, comparing the circumstances of the one having nothing but the rude apparatus of a new-born art suggested by himself, to that of the other, enjoying the advantage of eighteen months' improvements, Mr. Spencer is astonishingly correct, and his name should be identified with the discovery of these laws. The claim of originality involved in the inference drawn by Mr. Smee, though formidable at first sight, is nevertheless without foundation. Mr. Smee says—"These laws appear to me at once to raise the isolated facts known as the electrotype into a science, and to add *electro-metallurgy* as an auxiliary to the noble arts of this country." Unfortunately for the validity of Mr. Smee's claim, patents were taken out long previous, both in England and France, for the application of the electro-depositions to the arts. And Messrs. Elkington's patent for silvering and gilding by this process—a patent which has not yet been superseded—was not only published in full detail, but was in extensive operation months before the publication of Mr. Smee's book. Nevertheless, the publication of Mr. Smee's book did good service to the art of electrotyping; and the invention of his battery has so identified his name with the science, that it will go down to posterity as the name of an active and successful labourer in the field of electricity: to Mr. Smee we owe, moreover, the very appropriate name for the art, *Electro-Metallurgy*.

WORKS PUBLISHED ON ELECTRO-METALLURGY.—Besides many interesting papers in journals and magazines, several separate works were published on this art. Some months previous to the publication of Mr. Smee's work, Mr. Spencer had given the world *Instructions for the Multiplication of Works of Art in Metal by Voltaic Electricity*; and shortly after Mr. Smee's work appeared, we had, in rapid succession, Walker's *Electrotype Manipulation*, Sturgeon's *Art of Electrotyping*, Shaw's *Manual of Electro-Metallurgy, &c.*, all shewing much practical knowledge on the

subject. Walker's *Manipulation*, from its practical nature and its concise form, became the favourite of the amateur, and did more to popularise the art than all the others put together; and although little pretensions were made to originality, the author will not fail to have an honourable remembrance in the history of the art.

PATENTS TAKEN OUT FOR ELECTRO-METALLURGY.—So suddenly popular did electro-metallurgy become, and so numerous were the workers in the new art, and so eager was every one to find out something that was new in the mode of its application to manufactures, and to obtain a share of the benefits arising from the suggestion, that no less than ten patents were taken out for new applications, between the discovery of the art and the close of 1841; and not a year passed for a good many years after without adding patents for certain improvements, and applications of electro-metallurgy to some particular branch of manufacture, several of which will be noticed in their proper places; many of them, although based upon right theoretical principles, were, commercially speaking, entire failures, owing to practical difficulties not foreseen by the patentee affecting the economical working of the patent.

DESCRIPTION OF GALVANIC BATTERIES, AND THEIR RESPECTIVE PECULIARITIES.

NOMENCLATURE.—The terms that are employed to denote the various parts of a galvanic battery, and of other electrotype arrangements, frequently puzzle the student, and lead him into difficulties. Before we proceed to describe the various forms of the battery, we shall, for this reason, give a preliminary account of the nomenclature of galvanism.

The two extremities of a battery have long been called *Poles*; one of them the *Positive*, and the other the *Negative Pole*. But objections were taken to the use of the terms *negative*, *positive*, and *pole*, on the ground that such terms do not convey a correct idea of the circumstances or of the effects produced. Before connecting the two metals or extremities of a battery, there is no electricity evolved, nor is there any electrical tension on any part of the arrangement; and when the connection is formed the electricity simply makes a circuit; it is therefore supposed that no particular portion of that circuit can be said to be either negative or positive to another portion.

PROPOSED TERMS.—Various terms have been suggested as substitutes for negative and positive, and also for pole. The late Dr. Faraday proposed the following:—For pole, he substituted *electrode*, which signifies *a way*; for the negative pole, *cathode*, signifying *downwards*; and for the positive pole, *anode* or *upwards*. To understand these terms properly, we must suppose a battery lying upon the ground with its copper (positive) end to the east, and the wire connecting the ends of the battery bent into an arch similar to the course of the sun; the electric current will thus flow up from the east end of the battery, and descend into it at the west end. The fluid that is decomposed by a current of electricity passing through it was termed by Faraday an *electrolyte*; the elements liberated by this decomposi-

tion he termed *ions*, distinguishing those liberated at the cathode as *cations*, which in sulphate of copper would be the metal, and those liberated at the anode as *anions*, which would be the acid portion of the sulphate of copper.

The late Professor Daniell, disapproving of the terms cathode and anode, substituted *platinode* for the negative, and *zincode* for the positive pole. We think these terms are better adapted for electro-metallurgy than cathode and anode, which have no direct reference to ordinary conditions; while *zincode* distinctly expresses the substance dissolved, and *platinode* the element not acted upon.

The late Professor Graham adopted the terms *zincous* and *chlorous* poles, as synonymous with *zincode* and *platinode*, or positive and negative.

Although the terms positive, negative, and pole may not be the best, still, under all the conditions of electro-metallurgy, we deem them as appropriate for practical use as any of the proposed substitutes, some of which are based on supposed conditions which have not been proved, and may be found incorrect.

When we shall have occasion to use the two terms *pole* and *electrode*, these will be used synonymously: positive and negative electrode are synonymous with positive and negative pole.

Electrolyte will be applied to a solution undergoing decomposition by the electric current passing through it.

The *positive electrode*, or pole, is that metal in the electrolyte which is being dissolved, or, if not capable of being dissolved, at which the acid or solvent of the electrolyte is being liberated, as when sulphate of copper forms the electrolyte, the sulphuric acid is liberated. The *negative electrode*, or pole, is that metal or substance in the electrolyte upon which the metal is being deposited by the influence of the electric current, such as a medal upon which copper is being deposited in an electrotype process.

BATTERIES.

SINGLE PAIR OF PLATES.—If a piece of ordinary metallic zinc be put into dilute sulphuric acid, it is speedily acted upon by the acid, and hydrogen gas is at the same time evolved from its surface, having a disagreeable smell, arising from impurities contained in the zinc or acid. If the zinc be taken out, and a little mercury be rubbed over its surface, an amalgamation takes place between the two metals: the plate becomes of a beautiful bright silver appearance. If the

zinc thus amalgamated be again put into the dilute acid, there is no action, for the mercury retains the zinc with sufficient force to protect it from the acid. If a piece of copper be immersed along with the zinc, and the two metals be made to touch each other, a particular influence is induced among the three elements, zinc, copper, and acid; the acid again acts upon the zinc as if no mercury was upon it, but the hydrogen is now seen to escape from the surface of the copper; this action will go on as long as the two metals are kept in contact.



Fig. 3.

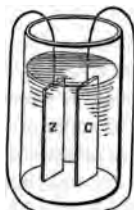


Fig. 4.

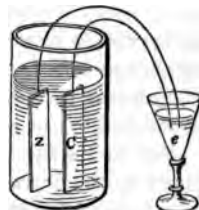


Fig. 5.

Fig. 3. represents the zinc and copper brought into contact, and placed in dilute sulphuric acid; in this experiment, gas will be seen escaping from the copper.

If, instead of causing the two metals to touch, a wire be attached to each, and the opposite ends of the wires are brought into contact outside the vessel, the same effect is produced (Fig. 4). If the two ends of the wires are placed in a little dilute acid in another vessel, the same action will take place between the zinc and copper as when they were in contact; but in this instance the ends of the two wires which dip into the vessel containing acid will undergo a change: the one attached to the zinc will give off a quantity of hydrogen gas, while the one attached to the copper, supposing it to be also copper, will rapidly dissolve (Fig. 5).

The copper and zinc, C and Z, with the acid in the first vessel (Fig. 5), constitute a battery of one pair. The wine glass e, with acid, in which the wires are placed, is termed the decomposition cell, the acid the electrolyte.

BEST KIND OF ZINC.—The zinc used for the battery should be *milled* or rolled zinc, not thinner than $\frac{1}{8}$ of an inch, otherwise the waste will be very great; for amalgamated zinc, when it becomes thin, is

so tender and brittle, that the utmost care cannot preserve it whole. The best thickness for the zincs, when their size is upwards of 4 inches square, is $\frac{1}{4}$ of an inch; but if under this size, $\frac{1}{8}$ to $\frac{3}{8}$ of an inch is the proper thickness. Cast plates of zinc should not be used, as they are negative to rolled zinc, and give less electrical power; besides, they are so porous that no amalgamation will protect them from the action of the acid—producing “local action,” as it is termed, which is not only a waste of zinc and acid, but prevents to a great extent the production of the quantity of electrical force which the surface of the zinc in use is calculated to give.

AMALGAMATION OF THE ZINC PLATES.—The amalgamation of zinc is a process exceedingly simple; nevertheless, if care be not taken, a very great loss in mercury and zinc is soon effected. A stoneware pan is the best to use, and should be sufficiently capacious to allow the zinc plate to lie flat within it: a mixture of eight parts water and one part sulphuric acid should be put into the pan, sufficient in quantity to cover the zinc plate, which should lie in it till the surface is perfectly bright. The pan is now raised on the one side, and a little mercury put into the lower part, care being taken that the zinc does not touch the mercury, to prevent which is the object of raising the pan on one side. A little coarse tow, tied to the end of a piece of wood, is dipped into the mercury, which lifts small portions of the metal mechanically, which is then rubbed with considerable pressure upon both sides of the zinc plate, over which the mercury flows easily: the plate is then washed, by dipping it into clean water, and is next made to stand upon its edge in another pan, with two small pieces of wood under it, so as to allow any excess of mercury to drain from it. In plating factories, instead of tow an old scratch brush is generally used. This is a brush made of fine brass wire, tied upon a piece of wood; but we prefer tow, as the brass wire amalgamates with the mercury, and causes a loss of that metal. After the zincs have drained for a few hours, the process should be repeated, only it is not necessary to allow the metal to lie in the acid in the second process previous to rubbing in the mercury: after draining a few hours the second time, amalgamation is completed. The results of amalgamating plates of zinc of the following size and $\frac{1}{4}$ of an inch in thickness were as follows: In the first process a plate, of 1 foot square, amalgamated on both sides, retained 3 ounces of mercury; but for the second process, the same size of plate only retained $1\frac{1}{2}$ ounces of mercury—in all $4\frac{1}{2}$ ounces for 2 square feet of surface.

Zinc rapidly absorbs mercury, which permeates the whole metal. If the mercury were in quantity, the zinc would dissolve in it; hence the propriety of rubbing the mercury into the zinc only in small portions; for if allowed to imbibe as much as it is capable of doing, it would not only be a loss of mercury, but the plate would become exceedingly brittle. When too much mercury is used, a portion of it will drop from the plate by standing, and carry with it some zinc dissolved in it, which creates loss and deteriorates the zinc plate.

The zinc in the battery, after being used, should never be allowed to lie in the acid when the battery is not in use, but should be taken out, and the surface carefully brushed, with a *hard* hair brush, in water, and then laid by in a safe place. The matter thus brushed off being an amalgam of zinc, should be carefully collected, and kept in dilute sulphuric acid, or in the waste acid from the batteries: most of the zinc in this amalgam will in this way dissolve out, so that a great portion of the mercury may be recovered; or by placing these brushings in a coarse cloth bag, and subjecting them to pressure in a screw-press, most of the mercury may, by this means be recovered.

ECONOMY IN AMALGAMATION.—If the battery is to be used seldom, and only for a short period at a time, or if the zinc is thin, another method of amalgamation may be adopted. The zinc plate, after lying in the dilute acid till the surface is bright, may be rubbed over with a solution of nitrate of mercury, which gives a very thin amalgamation; but this method is unsuitable if the battery is to be in use for several hours together.

When a battery is being worked daily, it will be advisable to repeat the amalgamation from time to time, otherwise local action will begin, and the working power of the battery be weakened, while the loss in zinc will be increased.

The following is the proportional rate of loss in zinc which we have found on the large scale under the most favourable circumstances. A new zinc plate, amalgamated as described, working continuously—

24 hours, zinc lost $12\frac{1}{2}$ ounces—copper deposited 12 ounces;
48 hours, zinc lost $20\frac{1}{2}$ ounces—copper deposited 17 ounces;
60 hours, zinc lost 34 ounces—copper deposited $24\frac{1}{2}$ ounces.

From these and similar data we found that the most economical way of using zincs is the following:—After being in the battery twenty-four hours, they are to be taken out, brushed, and laid aside for a short time or for a *shift*; after working other twenty-four hours, they are to be

again brushed and *immediately* re-amalgamated: if these directions are attended to, 1 ounce of mercury will be sufficient for 1 foot square of zinc both sides.

A plate of amalgamated zinc after being in use for twenty-four or more hours, and not to be required again for some time, should be re-amalgamated when removed from the battery, it may then stand over for days without injury; but if not re-amalgamated, and left exposed for several days, the zinc gets oxidised on the surface, forming a dry crust, and will not in this case re-amalgamate until this oxide is first dissolved off by a strong acid, causing considerable loss both of zinc and mercury; and if put into the battery without re-amalgamation, there is considerable local action and an imperfect current, until all the oxide is dissolved off, and a great loss of zinc.

The advantages of proper amalgamation will be made more evident in the sequel. We have only to add here, in consequence of an oft-expressed fear of the danger of working with quicksilver, that no apprehension need be felt: the skin does not absorb it, and there being no heat required in the operation that could convert the mercury into vapour, the only state in which it is dangerous, no salivation can take place.

DISTANCE BETWEEN THE BATTERY PLATES.—To return again to the battery-cell. It will be found that if the two metals—the zinc and copper in acid (Fig. 5)—be put very close to each other, the action will be much more rapid than when they are far apart. It will also be found that, allowing the zinc and copper to be kept at one distance, and the wires in the decomposition-cell at different distances, similar results will take place. When the wires are close the action in the battery-cell will be more powerful than when the two wires are put farther apart: these properties are applicable to all batteries and decomposition-cells of every kind. The following results will give an idea of the relations of these several conditions:—

1st. One pair of copper and zinc plates, measuring superficially 6 square inches, were immersed in a solution consisting of one acid to 35 water: plates of copper of equal size to those of zinc and copper were laid in the decomposition-cell, which was then filled with a liquid of equal strength to that in the battery-cell: the plates in the battery-cell and the decomposition-cell were then placed one inch apart: in four hours

The zinc in the battery-cell lost by dissolving $10\frac{1}{2}$ grains;
The copper dissolved in decomposition-cell 10 grains.

2nd. The battery plates were put 12 inches apart, and the plates in decomposition-cell 1 inch apart: in four hours

There were dissolved in the battery-cell, zinc 7 grains;
In decomposition-cell, copper 6 grains.

3rd. The battery plates were placed 1 inch apart, and the plates in decomposition-cell 12 inches apart: in four hours

The zinc in battery-cell lost $4\frac{1}{2}$ grains;
The copper in decomposition-cell lost $3\frac{1}{2}$ grains.

These results shew the importance of attending to the conditions of the respective agents, and also that distance of the electrodes in the decomposition-cell offers greater resistance than distance of plates in the battery-cell. The manufacturing electro-metallurgist will observe that the amount of work done in the same time when battery plates and electrodes are kept close together in their separate cells is in the one case double and in the other case triple that when the battery plates are far apart or the electrodes far apart. It also enables the workman to arrange the power of the current to the solution—the plates in a battery are generally at a fixed distance. Should the battery-power be too strong for the solution, or the article being coated be small, so that gas is evolved, by separating the electrodes to a greater distance this inconvenience is avoided.

DIFFERENT ELEMENTS OF BATTERIES.—Although our observations have up to this point been made on zinc, copper, and dilute sulphuric acid in the battery-cell, still these are not the only essential elements in a battery, as almost any two metals with a liquid similarly arranged will produce an electric current; but the current will vary according to the nature of the metals employed, and the effects produced upon them by the solution in which they are placed. If the exciting solution has the power of acting upon both metals, as when zinc and copper are immersed in dilute nitric acid, the current of electricity produced by the action of the acid upon the zinc will be neutralised to an extent corresponding to the relative action of the acid upon the copper. To have any effective electrical power, it is necessary that one of the metals employed be capable of combining easily with one of the elements of the solution in which they are placed, and forming a soluble salt, while the other metal does not; and the power obtained under proper circumstances has an intimate relation with these two properties in contrast. The metal

which undergoes solution is termed the positive metal, the other the negative metal. Metals are not considered to possess any intrinsic negative or positive principle; their relations in this respect are governed solely by the circumstances in which they may be placed. For instance, if we connect a piece of copper and a piece of iron, and immerse them in acidulated water, the iron is dissolved, and is positive in relation to the copper; but if the same metals are immersed in a solution of yellow hydro-sulphide of potassium, the copper is dissolved, and is positive relatively to the iron. Hence, to obtain a galvanic battery, the conditions are simply to provide two metals, and immerse them in a solution capable of acting upon the one and not upon the other. The first table shews the order in which the common metals stand to each other, in respect of their relative negative and positive properties, when immersed in water acidulated with sulphuric acid. The second table is given by Gmelin as the relations of the metals, in pure water and sea water, the most intensely negative metal standing highest, and the metal which acts most positively standing lowest:—

In Sulphuric Acid.	In Sea Water.
Platinum.	Platinum.
Gold.	Gold.
Antimony.	Silver.
Silver.	Copper.
Nickel.	Bismuth.
Bismuth.	Antimony.
Copper.	Iron
Lead.	Tin.
Iron.	Lead.
Tin.	Cadmium.
Cadmium.	Zinc.
Zinc.	

According to this arrangement, each metal is positive with respect to all that stand before or above it, and the electrical conditions of any pair become the more contrasted the farther apart they stand in the scale. Thus, a battery composed of zinc and platinum, if all else were equal, is much more powerful than one composed of zinc and copper; and again, copper and iron will make a very weak battery.

A battery may also be formed by having one metal and two kinds of liquids separated by a porous diaphragm. For example, we may have strong nitric acid in one division, and dilute sulphuric or muriatic acid in the other; and by putting into each a piece of clean iron, a powerful

current is obtained. The iron in the strong nitric acid will remain for a time unacted upon by the acid, while the iron in the dilute sulphuric acid will dissolve with great rapidity, producing a galvanic current between the two plates of iron, equal to that which would be produced by zinc and platinum in dilute sulphuric or muriatic acids. We give this as an illustration of the principle we have stated. These and several other arrangements of solutions and metals are expensive and troublesome to keep in order, and are therefore never used for practical purposes in the art of electro-metallurgy.

PROPERTIES OF METALS FIT FOR BATTERIES.—In looking to the preceding table, it may be asked, “Since lead stands next to copper in sulphuric acid, and is so much cheaper, why should it not be used instead?” The reason is, that there are other properties which a metal, especially one used as the negative element, ought to possess to fit it for use in a voltaic arrangement; such as the power of freely conducting an electric current, of keeping a bright surface, and not becoming oxidised—none of which properties belong to lead. Could that metal be kept from oxidising, a very effective current of electricity might be obtained by using it with zinc; but its surface soon gets coated with an oxide possessing none of the properties of the metal, and hence the arrangement becomes zinc and oxide of lead, which produces but a weak current of electricity. These remarks refer to any metal that is subject to oxidation—an occurrence which is often a source of annoyance to the electrotypist when using copper plates.

Lead slightly amalgamated, and used as the negative metal with zinc, produces a very constant current for a time.

Lead is also a very bad conductor of the electric current, which renders it unsuitable for an element in the battery, the negative metal being considered as only acting the part of a conductor: thus materially affecting the available power of an arrangement.

The following table shews the *relative conducting power* of the respective metals:—

Silver,	120
Copper,	120
Gold,	80
Zinc,	40
Platinum,	24
Iron,	24
Tin,	20
Lead,	12

From what we have just stated a battery composed of zinc and platinum, if all else were equal, will be more powerful than one composed of zinc and copper: this is true so far as regards their negative and positive tendencies; but so much does the conducting power of the negative metal affect the practical usefulness of a battery, that notwithstanding the fact that platinum is much more negative than copper, there is so much of the effective electricity expended in overcoming the resistance which the inferior conductivity of the platinum offers to the progress of the current, that a battery of zinc and copper proves to be a more effective and useful battery for electro-metallurgy than one made of zinc and platinum. The platinum, having only one-fifth of the conducting power of copper, will affect the practical value of a battery having platinum as the negative element, in the same way as described at page 30; by separating the electrodes, it weakens the effective power of the current for decomposing the solution, by offering it greater resistance. Hence, also, the reason that iron and copper, or iron and any other metal, makes but an indifferent battery—iron being a bad conductor; lead, as will be seen in the table, stands lowest in this property, and is therefore unsuitable for batteries, its conducting power being only one-tenth that of copper.

In fitting up a voltaic arrangement with a negative metal that is not a good conductor, such as platinum, the closer to the exciting liquid it is placed, in connection with another metal that is a good conductor, the better; the current obtained will be the more effective.

The following experiments will illustrate these remarks with a few of the common metals used as negative electrodes. There were in each battery six square inches of each metal exposed to the action of the acid, which was sulphuric acid diluted with twenty-five parts of water. The electrodes were copper of the same size, placed in sulphate of copper; and the quantity of copper deposited was taken as the data, each trial being of a different length of time:—

FIRST, IN ACTION HALF AN HOUR.	
BATTERY.	DEPOSITED.
Tin and zinc,	1·7 grains.
Copper and zinc,	1·8 „
Platinum and zinc,	·5 „
Platinised silver and zinc,	2·0 „
SECOND, IN ACTION TWO AND A-HALF HOURS.	
Tin and zinc,	5·9 grains.
Copper and zinc,	8·8 „
Platinum and zinc,	4·5 „
Platinised silver and zinc,	9·7 „

THIRD, IN ACTION SIXTEEN HOURS.

Tin and zinc,	54.5 grains.
Copper and zinc,	50.5 „
Platinum and zinc,	48.0 „
Platinised silver and zinc,	67.3 „

From these few experiments, it appears that tin and zinc, when used for a long time, constitute a very effective battery. It is very constant in its action, and thus suited for time. It stands next to platinised silver. The whole, in nineteen hours, gave respectively—

Platinised silver,	79. grains.
Tin,	62.1 „
Copper,	61.1 „
Platinum,	48.0 „

It may be mentioned here, as an illustration of the principles we are discussing, that in the platinised silver there is the negative and positive properties of platinum and zinc, with the conducting property of silver; and thus the two qualities are combined by a very ingenious contrivance, for which we are indebted to Mr. Smee.

BABINGTON'S BATTERY.—If we look back to the description given of the voltaic pile (page 2), and the improvement made upon it by Cruikshanks, we perceive the relation they bear to the pieces of copper and zinc mentioned in page 27; but the relation is more apparent in Babington's improvement upon Cruikshanks' battery. When working with this battery, it was found that the energy of the battery did not depend, as was supposed, upon the extent of surface of the zinc and copper in contact, but upon the extent of surface of these metals in contact with the liquid with which the battery was excited, and that it was sufficient if the zinc and copper touched each other in a single point—provided that the plates were plunged into the liquid, and that the copper plate be exactly opposite to a zinc plate in the same cell, a space being left between them. Hence, instead of soldering the zinc and

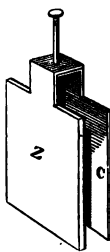


Fig. 6.

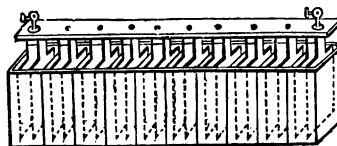


Fig. 7.

copper together, as Mr Cruikshanks did, it was enough to effect a communication by turning over a portion of the copper plate at the top,

and soldering it to the upper extremity of the zinc. Thus—c, the copper, is bent over to touch and be soldered to the zinc plate z. For this arrangement the wooden trough was divided, by plates of glass or varnished wood, into as many cells as there were pairs of zinc and

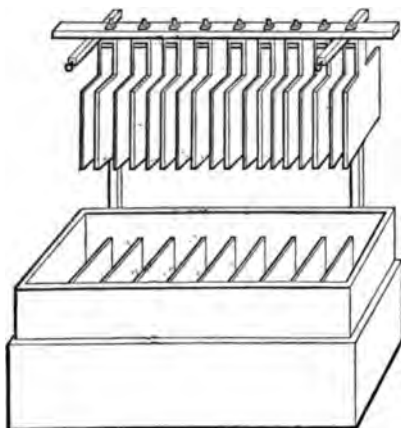


Fig. 8.

The cells being filled with the acid, or exciting solution, the metals were then placed into them in such a manner that each pair of zinc and copper plates had a partition between. By this arrangement the zinc of one pair faced the copper of the next pair in the cell, as shewn in Figs. 7 and 8. The former represents the plates immersed in the solution; the latter, the plates suspended on a rack over the solution. This arrangement was termed Babington's Battery.

WOLLASTON'S BATTERY.—Although we have spoken of the great value of amalgamated zinc for batteries, still, at the period when the arrangement just described was introduced, amalgamation was not known, and the zinc plates were therefore always liable to be destroyed by the acid. It was, consequently, of importance that no zinc should be exposed to the action of the acid that was not calculated to give electricity, as the energy of each pair of plates depends upon the extent of surface of the two metals *exactly opposite to each other*. It will be evident that in Babington's arrangement only one side of the zinc was effective in giving electricity, while both sides were exposed to the

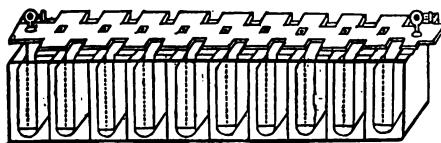


Fig. 9.

action of the acid. To obviate this defect, Dr. Wollaston caused the copper plate to *surround the zinc*, by which the whole surface of the zinc exposed to the acid was made effective in producing electricity, and thereby doubling its quantity without further cost. The accompanying figure (Fig. 9) shews the manner in which this battery was originally constructed.

This improvement, if we except several modifications of construction for the facility of taking the plates asunder for cleaning, &c., did all for this kind of battery that could be done.

MODIFICATION OF WOLLASTON'S BATTERY.—Wollaston's battery is still used in some factories for depositing metals, and it is found by experience to be both convenient and economical. The modification we found to be very suitable, and practically useful, may be thus described: In the arrangement represented in Fig. 9, when amalgamated zincs are used, small quantities of amalgam fall from the zinc plates upon the copper, which not only occasion local action, but the mercury amalgamates with the copper, spreads over it, and to a great extent lessens its efficiency; and as the copper must be made red-hot to expel the mercury, much loss of copper as well as mercury is the result. To obviate this defect, the copper is connected above the zinc and left open at bottom; as, for example, a thin sheet of copper, of dimensions according with the size of the cells in the battery, is cut thus (Fig. 10):—This copper is bent in the middle at *b*, the ends *aa* dip into the cells, while *c* is bent over to connect with the zinc plate of the neighbouring cell, thus—

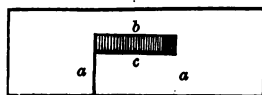


Fig. 10.

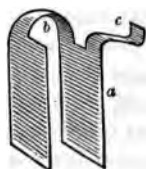


Fig. 11.

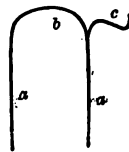


Fig. 12.

The zinc plates are placed between the bent copper *aa*. The following diagram of a battery of several pairs of plates will illustrate these observations:—

zzzz, The zinc plates;
cccc, Copper plates.

PPP, Partitions of trough, which are generally made of thin wood.

ww, Wires from battery.

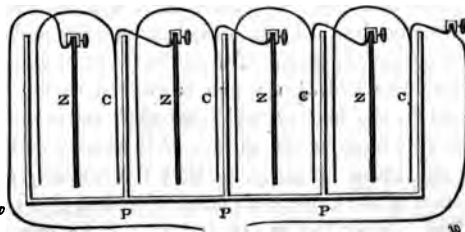


Fig. 13.

The zinc and copper are connected together by a binding screw. To construct this battery the zinc plates are put in first, being made to slide in grooves cut in the sides of the trough, the plates standing in the centre of their respective cells: the copper plates are put in, and the copper bands, marked *c*, are made fast to the zincs by binding screws, care being taken that the parts where they are connected are clean and bright, and that the copper and zinc touch nowhere else. A battery of nine pairs of plates can be fitted up and made ready for action in ten minutes.

In fitting up batteries of this sort, we are aware that sometimes great care is taken that the partitions in the trough are perfectly water-tight, and also formed of some non-conducting material, such as glass, or of wood, either pitched or saturated with some non-conducting substance; but we have found in practice that these precautions are not required, the principal thing to attend to being that the metals should not be allowed to touch, except at their proper connections: the partitions are a safeguard.

DEFECTS OF COMMON ACID BATTERIES.—Although we have spoken thus favourably of the principles upon which Wollaston's battery is constructed, still as a philosophical instrument it is far from being perfect, hence the many modifications of it which have been recommended. Indeed, electro-chemists, since the time of Volta, have been endeavouring to invent an instrument free from the defects which attach to Wollaston's—one capable of giving, at the same time, a constant and powerful current, abundant in quantity, and of great intensity. The success and results of these endeavours are so closely connected with the art of electro-metallurgy, and the knowledge of them is so essential to a successful prosecution of the art, that we must not be sparing in our descriptive details.

In operating with a Wollaston's battery, or any other arrangement composed of similar elements, such as zinc, sulphuric or muriatic acid, copper, and silver or platinum, it will be found that the current of electricity obtained diminishes in quantity and strength in proportion to the time of action. This is the result of various causes:—

1st. The hydrogen which is evolved at the surface of the negative metal in the battery, which we shall say is copper, adheres with considerable force to the surface of the metal, and consequently obstructs its superficial influence, so that the quantity of electricity which the surface of the two metals is calculated to give is much lessened.

2nd. After the battery is in action for some time, a portion of the

sulphate or chloride of zinc, formed in the battery by the solution of the zinc, becomes reduced upon the surface of the copper. This reduction is supposed by some to be owing to the electrolysation of the zinc solution by the passage of electricity; but it is more probably caused by a galvanic action upon the copper plate and the solution in the battery. In this way the sulphate of zinc formed in the battery, from its greater specific gravity, sinks to and accumulates at the bottom of the cell, so that after the battery has been in action for some time the lower portion of the battery solution is nearly neutral sulphate of zinc, while the upper portion is the dilute acid, so that the lower part of the copper plate in the battery is dipping into the neutral sulphate of zinc, while the upper part is in acid; hence a local galvanic action takes place between the upper and lower part of the copper plate. The result is the deposition of zinc upon the lower part of the copper plate. This deposition always begins at the lower edge of the copper plate, and spreads upwards, and thus weakens the electric current, both by this induced galvanic action between the zinc and the copper, upon which it is deposited, and by its tendency to send a current of electricity in an opposite direction to the main current, thereby neutralising to a great extent the original power of the circle.

3rd. When copper is used it becomes gradually covered over with a thin, black, slimy coating of oxide and other impurities, which materially affects the regularity and strength of the current: this is a source of considerable annoyance in working, and necessitates a regular cleaning of the coppers, which should be done immediately on being taken out of the battery, by brushing with a hard hair brush in water; but when the battery has been long in action, this mode of cleaning is insufficient: the plates are then required to be rubbed over with a little dilute nitric acid, and then washed. If the black coating be allowed to dry upon the coppers, they must be dipped into strong nitric acid till their surfaces are acted upon; or they may be moistened with a little urine, then brought to a dull red in the fire, and immediately plunged into water; but in both cases there is a loss of copper. A small quantity of the black matter, tested by us, gave oxide of copper, with iron, antimony, and lead, which are the general impurities of sheet copper.

Another source of weakness to the electric current, and which affects more or less all batteries of whatever construction, arises from the action of the acid upon the zinc. The more freely this action is allowed to proceed the more constant and powerful is the battery. The acid in combining with the zinc forms a salt, which, if it adhered to the surface

of the plate, would soon stop further action; but this salt being soluble in water, is dissolved from the surface of the plate as soon as formed, allowing a new surface to be exposed. But water can only dissolve a certain quantity of the salt, and its power of dissolving decreases as it approaches to the limit of saturation, hence there is a constant tendency to a decrease of power in the battery; and if means be not taken to withdraw the salt of zinc formed, the battery will continue to decrease in power, till at length it ceases to act. But long before the battery ceases to act, the presence of sulphate of zinc manifests itself in several ways, neutralising the efficacy of the battery. As already noticed, the zinc salt as it dissolves from the plate, being heavier than the acid solution, falls to the bottom; hence in a very short time the solution is formed of strata of different densities, and this induces a galvanic action between the lower and upper portions of the plates, both copper and zinc, and accounts for the deposition of zinc on the bottom part of both copper and zinc plates. This local galvanic action between the bottom and top parts of the zinc plate is sometimes so great when the battery has been long in action, as to double the thickness of the zinc plate at bottom, while the part near the surface of the solution is nearly penetrated by the acid; and when a battery is formed of a number of pairs, the terminal zincs are those most affected, the one forming the negative terminal or pole more so than the other. We have found a deposition of $6\frac{1}{2}$ ounces of zinc upon the two lower inches of a terminal plate, which measured in the solution 6 inches. The upper 4 inches of the plate gradually thinned to the surface of the solution, where it was not more than half its original thickness, the battery having been in operation but eighteen hours. When this occurs, the quantity of electricity circulating through the battery is very small. Although this evil may not proceed to the extent of having quantities of zinc deposited upon the bottom part of the plates, still the tendency to deposition, which every one who employs a battery for a long time must have observed, as also the more rapid action of the acid on the upper parts of the plates, shews that the action of the acid over the surface of the plate is very irregular, and consequently the quantity of electricity must be irregular in the same degree, often producing in the battery an intermittent action, which will be referred to further on.

Various means have been devised for removing the sulphate of zinc, and adding corresponding quantities of new acid water; the most simple and effective of which, according to our experience, is to make the battery trough much deeper than is required for the plates, which may be supported either by grooves in the side of the trough, cut to the pro-

per depth, or by a fillet of wood, or perforated false bottom; so that the zinc salt when formed may fall under the plates, and thus a much longer time elapse before its presence produces any decidedly bad effect. There can be no doubt, we think, that some easy means will yet be devised for carrying off the dense solution of sulphate of zinc before it rises to the plates, and for replacing it by acid water from above, thus giving to the battery a uniformity and steadiness of action it does not at present possess. There have been many ingenious contrivances tried for this purpose by the amateur, but we have seen none so simple and economical for manufacturing purposes as that referred to—battery-troughs twice the depth of zinc plates.

DANIELL'S BATTERY.—Some of the disadvantages now detailed were to a great extent overcome by a very ingenious arrangement discovered by the late Professor Daniell. The discovery consists in the separation of the zinc from the copper by a porous diaphragm, such as bladder, unglazed porcelain, &c., and the use of two distinct fluids. The portion of the battery containing the zinc is charged with dilute acid, but the portion containing the copper, or, what is most common, a copper vessel, is filled with a solution of sulphate of copper. The action in this battery is similar to that described in the ordinary battery: the zinc is dissolved by the acid, but the hydrogen, instead of being evolved at the copper plate, combines with the acid of the sulphate of copper: metallic copper is thus set at liberty upon, and adheres to the copper plate of the battery, improving its surface for the evolution of a current of electricity. From the constancy of the current maintained in this form of battery, it has been termed the *Constant Battery*. The construction of a single pair is described by Professor Daniell in the following terms:—

“A cell of this battery consists of a cylinder of copper, $3\frac{1}{2}$ inches in diameter, which experience has proved to afford the most advantages between the generating and conducting surfaces, but which may vary in height according to the power which it is wished to obtain. A membranous tube, formed of the gullet of an ox, is hung in the centre by a collar, and a circular copper plate, resting upon a rim, is placed near the top of the cylinder, and in this is suspended, by a wooden cross-bar, a cylindrical rod of amalgamated zinc, half an inch in diameter; the cell is charged with eight parts of water and one of oil of vitriol, which has been saturated with sulphate of copper, and

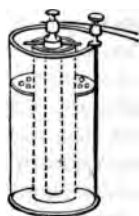


Fig. 14.

portions of the solid salt are placed upon the upper copper plate, which is perforated like a cullender for the purpose of keeping the solution always in a state of saturation. The internal tube is filled with the same acid mixture without the copper. A tube of porous earthenware may be substituted for the membrane with great convenience, but probably with some little loss of power." *

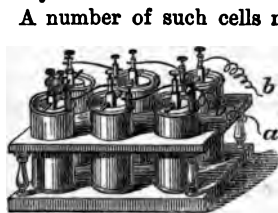


Fig. 15.

A number of such cells may be connected very readily by attaching the zinc of the one to the copper of the other, and (as shewn in Fig. 15) thus forming an intensity arrangement of great power and constancy.

This arrangement of battery is eminently suited to all kinds of electrical operations, and it may be borne in mind that it was by operating with this battery

the idea of electro-metallurgy first occurred. In this battery we see that the evils arising from the slow liberation of the hydrogen from the surface of the negative metal, and the deposition of the zinc upon the copper, and also the blackening of the surface of the copper, are all surmounted; but when the zinc solution becomes nearly saturated, which it soon does from the cell being small, the same results as stated above take place—viz., a local action between the lower and upper portion of the zinc plate or rod, and deposition of zinc on the bottom part, and extra dissolving of the upper portion, which rather diminishes than adds to the battery current—defects which are not so easily overcome in this as in the ordinary battery. However, the constancy of this battery over most of the others is indisputable. Nevertheless, it is not used to any extent in the art of electro-metallurgy, it being much less economical than the ordinary batteries, from the quantity of copper salt necessary to keep it in a working condition, and from the necessity of using porous diaphragms, which speedily wear out. If the diaphragm is made of animal membrane, the acid very soon destroys it; and although unglazed porcelain lasts a little longer, the acid acts upon the alumina, so that after a few days' working the diaphragm becomes too porous; and if the zinc plate touches the porous vessel, a circumstance very difficult to avoid, there is very soon formed in and upon the surface of the porous cell a deposit of copper, which speedily renders the cell useless, besides causing a loss of copper. The saturation of the zinc solution, already spoken of, not unfrequently produces the same effects—the saturated portion of the bottom becomes reduced by the local

* Daniell's *Chemical Philosophy*, 2nd edition, 1843, p. 504.

action, and thus often a minute point of metallic zinc touches the cell, and forms a nucleus for a deposit of copper upon the porous cell, which spreads over the surface very rapidly. Besides, there are always pieces of amalgamated zinc, like fine scales, falling to the bottom of the cell, which also form nuclei for the deposition of copper upon the porous cell.

After the cells have been some time in use, if they are laid aside and allowed to dry they are very liable to break. Care should be taken to keep them in clean water till the salts within the pores are dissolved out; and if this precaution is taken they may be preserved for a long time, if they are only used occasionally.

The remarks upon the economy of the arrangement just described have reference to its use as an instrument, or separate battery, for the deposition of a metal in a separate cell (decomposition cell); but not to the arrangement known in electro-metallurgy as the *single cell* process, which is simply a modification of one pair of Daniell's arrangement; a description of which, with its comparative economy, will be given in another part of this treatise.

Professor Daniell says that any depth of cell may be used according to the power required; but this cannot be done with equal advantage, for a large surface of zinc in a cell is not the most economical, when quantity of electricity is required.

GROVE'S BATTERY.—Another battery, constructed upon the same principle as Daniell's, but differing in the arrangement of the metals, and the substances used to excite them, was invented by Mr. Grove, and is known as *Grove's Battery*. In this arrangement platinum is used instead of copper, and strong nitric acid instead of the sulphate of copper of Daniell's battery. One pair may be fitted up conveniently in a tumbler or jelly-pot. A hollow cylinder of zinc is placed inside the tumbler; within this cylinder is placed a porous vessel, in which is a slip of platinum, either in sheet or foil; the porous vessel is filled with strong nitric acid, and the tumbler with dilute sulphuric acid; a wire is next attached to each metal, and the battery is complete. When a series of pairs is to be used, the form we have found most convenient is to arrange the metals in the same manner as we have described for Wollaston's trough (page 37). The zinc is formed in the same shape as shewn by fig. 11. The zinc is placed in the cell of the trough, and the porous vessel, which should be flat, is placed within the zinc, so that the platinum in it may be connected with the zinc of the neighbouring pair, as represented in fig. 16.

zzz, Are the zinc plates of the form of fig. 11.

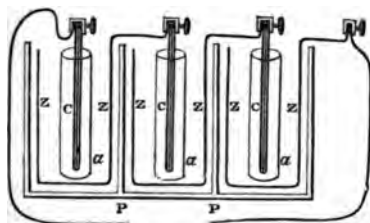


Fig. 16.

aaa, Porous cells filled with nitric acid.

ccc, Plates of platinum united to the zinc at top by binding screws.

pp, Are partitions. The divisions of the battery trough need not be water tight, but merely such as will prevent the zincs from touching one another.

It will be seen that by this means any number of pairs may be easily arranged. Care, however, must be taken, when fitting up such an arrangement, that the platinum be kept closely connected with the zinc by a large surface, otherwise the platinum will be fused at the connections. A flat piece of wood, with a groove to fit the zinc, is often made the means of keeping the two metals together; but we prefer flat binding screws of brass, for if kept clean they assist the connection, being good conductors. The fusion of the platinum connections, a practical and often expensive annoyance, may, however, be completely prevented by coating about half an inch of the end of the platinum either with copper or silver, which is easily effected by the electro-process—the coated part is then connected with the zinc by any convenient means without the risk of fusing.

This form of battery is also free from some of the objections to the common battery, but it is seldom or never used in the ordinary processes of electro-metallurgy. Its advantages over every other form of battery described are its great activity of action and intensity or power of current—a circumstance not generally sought after by electro-metallurgists. But if it were duly considered that a battery consisting of three pairs of zinc and platinum is far more effective than an ordinary battery of ten or twelve pairs (although the elements of its construction are more expensive), it would stand a fair chance of being adopted as the more economical battery of the two.

The porous cells have not the objection of being closed up by the deposition of metals upon or within them; but they are affected by the acids, and by long working they become too porous, the nitric acid passing through and causing rapid destruction of the zinc. It wants the constancy of Daniell's, its quantity declining rapidly when long in action—one feature we have often experienced which we have not seen observed by other experimenters. When working with a Grove's battery

of from eight to twelve pairs, the platinum being six inches by seven inches, after the battery was in action for four or five hours, during which it diminished in quantity gradually, all of a sudden it seemed to recover its energy, giving a quantity and power not much less than it gave in the first hour, and then declined again rapidly, but occasionally renewing its vigour for short periods. We have thought it probable that this

of nitrate of ammonia in the
 iring the first action of the
 e-acted upon.

1 to the use of this arrange-
 also for many experimental
 ch corrode everything within
 and hurtful to every person

rove's, and is much used for
 ead of the platinum. One
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 which gives great compact-
 and dilute acid is placed in
 s or stoneware vessel charged
 der and zinc are connected,
 re simple and less expensive
 a solid bar of carbon or coke
 hich is placed in a stone or
 iving a hollow cylinder of zinc
 t one inch of space between
 ill's. This form of battery is
 sed for some purposes by the
 volved from this battery also.

a the common battery of zinc
 and copper were much lessened by an ingenious contrivance of Mr.
 Alfred Smee's. This gentleman had observed that if the copper plate
 of the battery be roughened, either by corrosive acids or by rubbing
 the surface with sand-paper, its action was made much more efficient,
 the rough surface evolving the hydrogen much more freely. Taking
 advantage, therefore, of this observation, he covered platinum foil with a
 finely divided black powder of platinum, deposited by electricity from
 a solution of that metal, and used this in place of the copper in the
 ordinary battery. Instead of platinum foil, Mr. Smee soon after adopted

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silver foil, which is much less expensive. The method of preparing these plates is given by Mr. Smee as follows:—"The silver to be prepared for this should be of a thickness sufficient to carry the current of electricity, and should be roughened by brushing it over with a little strong nitric acid, so that a frosted appearance is obtained. It is then washed and placed in a vessel with dilute sulphuric acid, to which a few drops of nitro-muriate of platinum has been added. A porous tube is then placed into this vessel with a few drops of dilute sulphuric acid; into this tube a piece of zinc is put, contact being made between the zinc and silver; the platinum will, in a few seconds, be thrown down upon the silver as a black metallic powder. The operation is now completed, and the platinised silver ready for use." A simple method, which obviates the use of a battery, is thus described: Lay the silver between two pieces of sand-paper, and press it with a common smoothing iron, then pull the silver out while under the pressure. The platinum solution is made very hot, and the silver dipped in it for some time, which affects the coating.

The nitro-muriate of platinum is easily prepared: take one part of nitric acid, and two parts of hydrochloric acid (muriatic acid); mix together and add a little platinum, either as metal or sponge; keep the whole at or near a boiling heat; the metal is then dissolved, forming the solution required.

Several experiments have been tried with a view to substitute a cheaper metal than silver to deposit the platinum upon, but not with much success. Cheap metals have also been coated with silver by the electro process, and then used for depositing the platinum upon.

The most successful is a composition metal made of tin, lead, and a little antimony, rolled into sheet and plated by silver; this was found very convenient, because it could be easily bent into any required shape, and it keeps its place without the necessity of fixing in frames, as required by thin silver; nevertheless, for constant work these plates are found not to present any permanent advantage, and have been abandoned; besides, to give a sufficient coating of silver becomes as expensive as silver foil.

Mr. Smee, in constructing his battery, has been guided by the expense of the silver, and therefore reverses the order of arrangement introduced by Wollaston, by surrounding the platinised silver with the zinc. Fig.

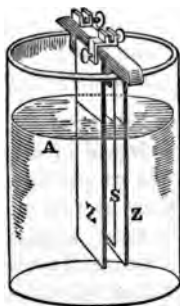


Fig. 17.

17 represents a single cell of this form of battery. A, is the jar containing the solution. zz, the two amalgamated zinc plates. s, the platinised silver plate. The whole are suspended by a cross bar of wood; and as it is essential to the proper working of the battery that the plates be always parallel to one another, the wooden frame is generally extended round the edge of the thin silver plate, though it is not so represented in the figure. One of the clamps at the top of the wooden bar is connected with the platinised silver plate, and the other with the pair of zinc plates. Instead of a glass or stoneware jar, small square troughs, made of gutta percha, are often used for the Smee's battery, as they suit admirably, and are not liable to break.

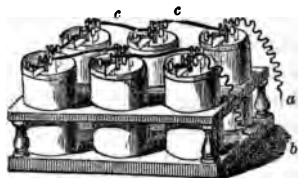


Fig. 18.

When *intensity* of electricity is required, it is necessary to use a number of such cells, which may be arranged in a wooden frame, in the manner shewn in Fig. 18, where *ab* represent the two poles of the battery, and *cc* the wires by which the cells are connected with one another.

A superior form of compound Smee's battery, contrived by Acland, is represented in Fig. 19. In this apparatus the plates are all connected

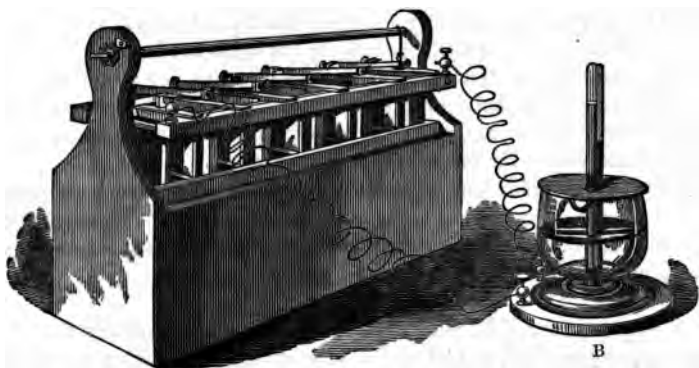


Fig. 19.

to a frame that can be elevated or depressed by means of an iron rod and ratchet wheel, so that the plates may be either partially or entirely immersed in the solution, or raised at pleasure out of it. The con-

nections are so contrived, that by a slight alteration the battery is adapted to afford either *quantity* or *intensity* of electric power. It is usually made to contain six cells, any number of which can be used at once, either singly or in whole, as a given process may require. The exciting fluid is contained in an incorrodible stoneware trough, placed in a mahogany box. A battery of this description, each silver plate of which measures 20 square inches, has sufficient power, when decomposing water, to disengage 1 cubic inch of mixed gases in 50 seconds, and may be used for other electrical purposes requiring power.

Letter B, in Fig. 19, represents an apparatus for shewing the decomposition of water into oxygen and hydrogen gas by the voltaic battery.

It will be observed in Smee's arrangement that there are two surfaces of zinc in every pair exposed to the acid, which do not give off any electricity. When long in use, these are much acted upon, forming a consideration of some value to a manufacturer.

The silver used is very thin, and liable to crack when taken from its frame, and therefore not so easily made into different constructions as we can do with copper. It is also liable to have zinc deposited upon its surface when long in action; and when in constant use and requiring to be taken to pieces every night for cleaning zinc, &c., it is not so handy, and more liable to hurt by a workman than the ordinary battery.

There is, we believe, no arrangement of battery better known and more used by amateur electrotypists than Smee's, and there are probably none better adapted for small operations; but it has not been introduced to any extent in the factory. When used in series, the advantages it possesses over Wollaston's do not counterbalance the extra labour and expense attending its use, and many who have tried it in the operations of the factory have for these reasons given it up.

Numerous modifications of these different batteries have been proposed from time to time, and also other kinds of battery, intended for different objects, but those given embrace all that are used for electro-metallurgical purposes.

EARTH BATTERY.—In the early history of electro-metallurgy the art became very popular, and all who were working at it, whether for profit or amusement, were eager to find out some improvement in the operation, either for cheapening the process or simplifying the manipulation; so that when it was found that a piece of copper and a piece of zinc imbedded in the earth, and connected by a wire, gave a current of

electricity in the same way as if they were placed in any battery trough, instantly suggested the application of the earth, in this way, as a battery for the purposes of depositing. We remember of an offer made to a manufacturing electro-metallurgist of an exclusive right to work this form of battery for their depositions; and the principle of the battery insisted upon by the patentee was, that there were constant currents of electricity passing through the earth, and by burying a sheet of copper and a sheet of zinc a few feet apart, and connecting them by a wire which, being a better conductor than the earth, induced the natural current to pass through it, thus giving an inexhaustible supply of electricity. This idea was so attractive to the party negotiating for the patent right, that nothing less than a series of experiments, with large sheets of copper and zinc in different fields and localities, would satisfy them. We need hardly say these trials were without success. The electricity obtained in this way is very weak, depending wholly upon the moisture of the earth, and is simply a water battery. It would be unnecessary to enter into details of our trials with large and small sheets of zinc and copper, and these placed at distances of from a few inches to hundreds of feet apart, further than to say that we made electrotypes by this means, and also plated small articles with silver, but the action or deposition was very slow. We obtained a greater amount of deposition in five minutes from one square inch of zinc and copper placed in dilute sulphuric acid, than from four feet of zinc and copper placed in the earth for the space of an hour. An earth battery adapted to deposit from 150 to 200 ounces of silver per day would require acres of land and tons of zinc and copper for batteries.

In this, as in all other forms of battery, the deposit is in relation to the zinc oxidised in the battery: there would, therefore, be no economy in using the earth battery in single pairs, and to use an intensity arrangement would add to the expense, as it would require upwards of one hundred pairs thus arranged in the earth to be equal to three or four pairs of the same size of Wollaston's for the object of depositing, and would thus be adding to the cost of depositing one hundred times the equivalent of zinc, instead of four times its equivalent.

GENERAL REMARKS UPON BATTERIES.—The temperature of the place in which batteries are kept affects their working power to a considerable extent; heat increases and cold diminishes their action; so that although the batteries should always be so situated that the gaseous fumes from them will escape into the open air; still, if put outside and exposed to the weather, there is a tendency to irregular action: their effective

power is greatly retarded by cold. Where it can be adopted, the batteries should be kept in a place where the temperature can be kept at between 60° and 70° Fahr., in which case the amount of work done will be regular, and the fumes should be carried away without going into the apartment where people are working.

MAGNETO-ELECTRIC MACHINE.—Mr. Woolrich, of Birmingham, was the first to apply the magneto-electric current, instead of voltaic electricity, to the purposes of electro-metallurgy. We cannot speak of Mr. Woolrich's machine from experience; but, from a statement made at the meeting of the British Association in 1850, by Mr. Elkington, of Birmingham, who is the proprietor of the patent, and a gentleman of most extensive experience, it would seem that he had up to that time never been induced to give up the ordinary battery in favour of magnetism, or any other suggested improvement. However, this means of obtaining electricity for the purposes of electro-metallurgy has been much improved by forms of magnets, &c. The first improvement published was by Mr. Millward, and described by him as follows:—“The first branch of the improvement is carried into effect by the employment of an electro-magnet, formed by a current of electricity produced from a magneto-electric machine, instead of that generated in a voltaic battery; and such an electro-magnet may be very advantageously used for magnetising large bars of steel, or for producing very powerful magnets. Any of the known forms of magneto-electric machines will serve thus to convert a bar of steel to an electro-magnet; but the patentee prefers to use one composed of four, eight, or any other number of permanent magnets, having double the number of armatures, and coiled with strong wire of about 60 feet in length. The machine about to be described has been found to answer well in practice. In this machine the steel magnets are composed of eight plates of a U form, weighing about 30 lbs. each plate; and there are eight such compound magnets, all the north poles of which are arranged on one side of the machine, and the south poles on the other side, although this precise arrangement is not essential, and may be varied. The armatures are of soft iron, weighing about 15 lbs., and are coiled about with 60 feet of copper wire, of No. 4 gauge, and insulated in the usual manner. The armatures revolve in a brass wheel, and are caused to pass as near to the poles of the magnets as practicable, the commutator or brake acting on the whole eight magnets at the same instant, so that the current of electricity shall always pass in one direction, and the surfaces of the whole of the sixty-four plates be

in combination at the same time. The bar of soft iron used as the electro-magnet with this machine weighs about 500 lbs., and is coiled with bundles of about thirty copper wires of No. 16 gauge, and about 60 feet in length (the bundles are formed by binding a series of uncovered wires together into one covered strand or bundle), and the power of the electro-magnet will depend upon the power of the permanent magnets used in the machine, both as to the weight it will support from a keeper and as to its capability of rendering bars of steel permanently magnetic by contact therewith. It will, therefore, be evident that by having two sets of the permanent magnets, and changing them in such machine, their supporting power may be increased by continued charges or passes from the electro-magnet thus produced. In one form of electro-magnetic machine, represented and described under the second head of the invention, the steel bars or permanent magnets are eight in number (these bars may be of cast or soft iron; but when soft iron is employed, bars of steel permanently magnetised will have to be used in conjunction with them), of a U form, and arranged around a circle, with their poles pointing towards the centre. Each arm of each of the magnets has attached to it straight bars of steel, also rendered permanently magnetic (of which any desired number, and of any length or size, may be employed, according to the strength of magnet required), which are so placed as to be out of the influence of the armatures when the latter are revolving. The poles of the U-shaped magnets are, on the contrary, as nearly as possible in contact with the armatures which revolve within the circle formed by them, either between the poles or in front of them. Instead of the bars which form the circle being of steel and magnetised, they may be made of soft iron, and depend for their magnetism upon the magnetic bars before-named placed around them. In another form of machine both the magnets and armatures are stationary, and the commutator alone has motion between the poles of the horse-shoe magnets and the armatures, being mounted on a spindle and caused to revolve by a band from some driving machinery. The commutator, or brakepiece, is composed of a brass centre, with four radial arms of soft iron, either solid or formed of two or more plates."—See *Repertory of Patent Inventions*, vol. xviii., for 1851, and Sketches therein.

The quality of these machines for depositing depends much upon their sustaining power. Eight of these sets of plates or magnets, containing altogether about 12 cwt. of steel, in a proper state of working, are said to form a battery capable of depositing from 12 to 20 ounces of silver per hour.

The most effective and useful improvement made upon the electro-magnetic machine we have seen is that by Mr. Wilde. Mr. William Crooks, in the *Journal of Science* (1866), gives an exhaustive description of this machine, from which we make the following extract:—

“The principle of the machine can be expressed in a few words: it consists in the application of the current from an electro-magnetic machine, armed with permanent magnets, for the purpose of exciting a powerful electro-magnet—this electro-magnet being now used as the basis of a still larger electro-magnet machine, for the purpose of having induction currents produced by its agency. In other words, by well-known means an electric current can be obtained by the rotation of an armature close to the poles of a magnet. If this electric current be passed round an electro-magnet, it may be made to produce a far greater amount of magnetism than was passed by the first magnet. There is no difficulty, therefore, in comprehending how, by the mere interposition of a rotating armature and the expenditure of force, a small and weak magnet may be made to actuate a very powerful magnet: but as the power of the magnet increases, so does the power increase of the electric current, which may be generated by induction in an armature rotating between its poles.

“The weight of the electro-magnet of the 10-inch machine is nearly 3 tons, and the total weight of the instrument is about $4\frac{1}{2}$ tons. The machine is furnished with two armatures, one for the production of ‘intensity,’ and the other for the production of ‘quantity’ effects. The intensity armature is coiled with an insulated conductor, consisting of a bundle of thirteen No. 11 copper wires, each 0.125 of an inch in diameter; the coil is 376 feet in length, and weighs 232 lbs. The quantity armature is enveloped with the folds of an insulated copper-plate conductor 67 feet in length, the weight of which is 344 lbs.

“With the three armatures, driven at a uniform velocity of 1500 revolutions per minute, an amount of magnetic force is developed in the large electro-magnet far exceeding anything which has hitherto been produced, accompanied by the evolution of an amount of dynamic electricity from the quantity armature, so enormous as to melt pieces of cylindrical iron rod fifteen inches in length, and fully one quarter of an inch in diameter, and pieces of copper wire of the same length, and one-eighth of an inch in diameter.

“The extraordinary calorific and illuminating powers of the 10-inch machine are all the more remarkable from the fact that they have their origin in six small permanent magnets, weighing only 1 lb. each, and only capable at most of sustaining collectively a weight of 60 lbs.

When working up to its full intensity, it requires an engine of about 7 horse-power to drive it."

More recently M. Gramme has constructed an electro-magnetic machine of a somewhat different form, a description of which is given in *Nature*, vol. xii., from which we extract the following:—

"These machines weigh 750 kilogrammes, and the weight of copper used in their construction is about 175 kilogrammes. With a small engine of one horse-power, one of them will deposit 600 grammes of silver per hour ($19\frac{1}{4}$ oz.) By some recent modification in its construction, this machine has been improved so as to increase the weight of silver deposited per hour to 2100 grammes, or above $4\frac{1}{2}$ lbs."

In this statement no mention is made as to the size of the electrodes on which this quantity of silver can be deposited, as that is of great consequence, and also the arrangement of these electrodes. However, such machines as the above cannot but be of great consequence to a manufacturing electro-metallurgist, whose business is so extensive as to warrant the expense of the first cost; but in the ordinary operations of plating and gilding, the construction of the battery is so simple, and the immediate outlay so small, that only a few in the trade have as yet adopted the electro-magnetic machines. Where there is intensity accompanied with quantity, the intensity may be utilised by an arrangement of the electrodes, as referred to at Fig. 35.

Before concluding the description of batteries, we may briefly notice one or two little conveniences which are indispensable to the operation. The first of these is what are termed *binding screws*, by which the parts of batteries, as we have shewn by numerous figures, are connected

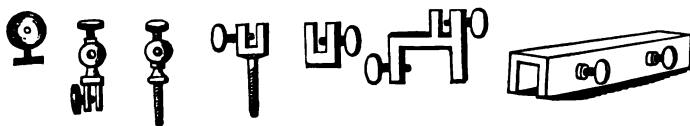


Fig. 20. Fig. 21. Fig. 22. Fig. 23. Fig. 24. Fig. 25. Fig. 26.

together, or by which their poles are connected to the objects through which the voltaic current is to be passed. They are usually made of brass, and of various forms, according to the shape of the objects that are to be connected.

Figs. 20 to 26 represent some of the most useful kinds; Fig. 20 is used to connect wires together; Figs. 21 and 25 are required for Smee's battery (see Fig. 17); Figs. 24 and 26, to connect the plates of Grove's battery; Figs. 22 and 23 are used for Daniell's battery. In all cases,

the parts that touch the surfaces to be connected must be perfectly clean and bright.

In many cases, when operating with weak currents, it is desirable to

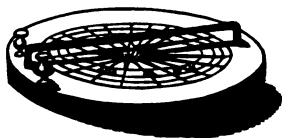


Fig. 27.



Fig. 28.

ascertain whether there is a current, and its probable strength. This is easily determined by means of a galvanometer, two varieties of which are represented by Figs. 27 and 28.

A galvanometer is a magnetic needle surrounded by a copper wire in the direction of the needle. When a current of electricity passes through this wire the needle will turn round until it stands at right angles to the wire or electric current. A needle resting upon a point, as Fig. 27, of some weight, requires a stronger current to move it than one very fine and light suspended by a silk thread, as Fig. 28, will. The latter will stand at right angles when the current of electricity is too weak to decompose a solution of sulphate of copper.

ELECTROTYPE PROCESSES.

SINGLE-CELL OPERATIONS.—We shall now proceed to detail the process of electrotyping, the materials for which are of the most simple nature. Let us suppose that the object of the student is to copy a copper medal—for example, the side of a penny-piece. Dissolve a quantity of the crystals of sulphate of copper in any convenient vessel; if distilled water can be had, the better. This is conveniently done by suspending the crystals in a coarse cloth on the surface of the water, or the crystals may be put into the water, and well stirred till dissolved; crushing the crystals facilitates their solution. The water should be kept cold, and be fully saturated with the salt, and the solution allowed to stand untouched for several hours. This last precaution is not always essential, but only necessary when the copper solution is not perfectly clear and transparent.

The sulphate of copper of commerce has often a large quantity of iron in it, a portion of which becomes per-oxidised, and will precipitate or fall to the bottom of the solution on standing; indeed, when it is known that the salt contains much iron, it is best to crush the salt very fine, and expose it to the air for some time; when dissolved, after this exposure, a great quantity of iron will settle to the bottom, the solution should be carefully decanted, and the last portion filtered. The clear saturated solution should now have about one-fourth more water added to it, as a completely saturated solution is not the best. A newly-formed solution does not deposit so freely as one that has been in use for some time. The addition of a few drops of sulphuric acid, or, what we have found better, a little sulphate of zinc—about one ounce to the pound of sulphate of copper—improves the condition of a new solution.

Next, put the solution of sulphate of copper into the vessel intended for use, say it is a large jelly-pot, in which let a vessel of unglazed porcelain (porous vessel) be placed, filled to within half an inch of the mouth with a mixture of twenty-four parts water and one sulphuric acid, taking care that the copper solution is of the same depth as the solution in the porous cell.

PREPARATION OF THE COIN.—A fine copper wire is now put round the edge of the coin or medal, and fastened by twisting. Or, if the wire cannot be fastened round the edge of the coin, take a thin strip of copper, about half-inch broad, clean the back of the coin and the portion of the slip to be laid upon the coin, put the two surfaces together, press them tight till you pour a little bees'-wax over them, and when it solidifies it will hold the two surfaces together; or a strip of gum paper put over them will keep the two surfaces together. Then cover the whole back part, including copper slip, upon which the deposit is not required, with bees'-wax or tallow, or, what is better, imbed the back of the coin in gutta percha. Have the fore part or face, upon which the deposit is required, well cleaned, and the surface moistened with sweet oil by the aid of a camel's hair pencil, and then cleaned off with a silk cloth till the surface appears dry; or, instead of oil, the surface may be brushed over with blacklead, which will impart to it a bronze appearance. The use of the oil or blacklead is to prevent the deposit from adhering to the face of the coin. A very common method

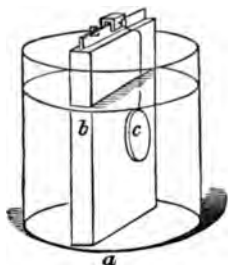


Fig. 29.

to prevent the copper deposit adhering to the copper mould is this:—Take a gill of rectified spirits of turpentine, and add to it about the size of an ordinary pea of bees'-wax. When this is dissolved, wet over the surface of the mould with it, and then allow it to dry: the mould is then ready to put into the solution. Medals taken from moulds so prepared retain their beautifully bright colour for a long time. But when fine line engravings are to be coated, the little wax dissolved in the turpentine may be objectionable; so also is blacklead, for both

have a tendency to fill up the fine lines. In this case, let the wash with turpentine be wiped off by a silk handkerchief, instead of drying it; but for ordinary medals this objection will scarcely apply. This being done, the opposite end of the copper wire round (or slip attached to) the penny-piece is to be connected with a piece of amalgamated zinc, either by means of a binding screw or a hole in the zinc. Then place the zinc in the acid within the porous cell, and put the penny-piece into the copper solution; bring the face of the coin parallel to the zinc, at the distance of about half an inch or one inch from the porous vessel. Deposition immediately begins, and the metal thickens according to the length of time the action is kept up (Fig. 29). In about twenty-four hours the deposit will be of the thickness of a common card, and it may then be

taken off. The zinc is to be brushed and washed before it is put aside. The wire or slip attached to the coin is now to be removed, and the wax, or whatever has been used to prevent the deposit going upon the back, is melted off. Should any particles of copper be deposited upon the edge of coin or medal, these are to be removed or rasped off with a pen-knife, after which the deposit is easily separated from the coin: it will be found a perfect counterpart of the face of the penny-piece, forming a mould.

This mould is next to be treated exactly as described for obtaining it from the penny-piece, and the deposit from it will be a *fac-simile* of one side of the penny-piece or medal. With care, any number of duplicates may be taken from this mould.

It need hardly be remarked, that as copper is deposited the solution becomes proportionally exhausted, and in a short time the current of electricity passing will be too much for the strength of the solution, which will then give a deposit of a sandy consistence without tenacity.* It is therefore necessary, while the deposition is going on, to suspend some crystals of sulphate of copper at the top of the solution, which, as they dissolve, will maintain its strength.

FORMS OF APPARATUS.—We have referred to a jelly-pot and porous cell, but it will be observed that no particular form of apparatus is required for electrotyping, but certain modifications may be adopted for convenience and economy. As every portion of the zinc in the acid is capable of giving off electricity, by placing the cell that contains the zinc in the centre of the copper solution moulds may be suspended on each side of that cell (Fig. 30). We have also observed (see Daniell's battery) that the zinc plate should not be allowed to touch the cell, as the copper will be reduced upon it and the cell destroyed. To avoid this, a thin piece of wood is placed at the bottom of the cell, and the zinc allowed to rest upon this.

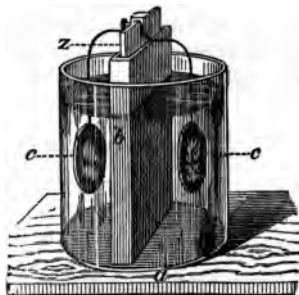


Fig. 30.

Instead of porous vessels made of earthenware, a bladder may be used, in which the acid and zinc are placed. We have also seen a vessel prepared for this purpose with a groove in centre, into which

* See Laws of Deposition, page 21.

was placed a porous partition—either a plate of biscuit porcelain, plaster of Paris, very thin sycamore wood, or dressed skin fixed upon a frame. The porcelain, as before-mentioned, is the best; plaster is too porous, and the solution soon destroys it; wood is too close, and the deposit is consequently very slow; skin does very well for a short time, but it is soon destroyed. When porous cells were not convenient, we have made electrotypes by wrapping the zinc plates in two or three folds of stout cartridge-paper, moistened with a solution of salt, and placing this in the copper solution with the mould. Of course, this is only to be adopted when a porous vessel cannot be obtained. The paper lasts but a short time, and has therefore to be frequently renewed; besides which, there is always a deposit of copper upon the paper, thus occasioning a loss. We have found common coarse garden-pots answer excellently for porous vessels, closing the aperture at bottom with a cork.

The precautions that have been given (see Daniell's battery, p. 41) as to the preserving of the porous cells when not in use, are applicable to the cells or partitions used in these processes, which, when not in use, should be kept in water, or should not be allowed to dry until they have been in water long enough to dissolve out the salts that were within the pores of the cell; otherwise the salts crystallise, and either crack the cell or cause it to scale off in small pieces. Porous cells, when not thoroughly washed and freed from salts, if laid aside for a few days, often throw out an efflorescence, or crystalline growth, like mould upon paste, of a soft silky texture, and from one-half to one inch in length. An analysis of this efflorescent matter gave—

Oxide of zinc,	39.6
Sulphuric acid,	26.0
Water,	34.2
						<hr/>
						99.8

COMPARATIVE VALUE OF EXCITING SOLUTIONS.—We have recommended the porous cell being filled with dilute sulphuric acid, which we consider best; but other saline solutions will serve the same purpose: solutions of common salt, salammoniac, and sulphate of zinc have been recommended, and each has been called best in its turn. The following results of experiments with these solutions in the porous cell will shew their relative qualities, and enable the student to judge for himself. The size of the zinc in the liquid used in these experiments measured six inches by six inches; the copper plates upon which the deposits were

formed were the same size; the solution of copper was kept at the same strength; the time that each was in solution was sixteen hours. The sulphuric acid used in these and in other experiments to be cited is concentrated, equal to 167° Twaddell.

Solution in Porous Cell.	Zinc Dissolved.			Copper Deposited.		
<i>Salammoniac.</i>	Oz.	Dwt.	Gr.	Oz.	Dwt.	Gr.
Saturated solution,	1	5	14	1	2	12
1 part saturated solution,	1	8	5	1	3	10
1 part water,						
1 part saturated solution,	0	12	13	0	10	17
3 parts water,						
<i>Common Salt.</i>						
Saturated solution,	0	16	3	0	14	12
1 part saturated solution,	0	18	9	0	17	8
1 part water,						
1 part saturated solution,	1	0	5	0	19	16
3 parts water,						
<i>Sulphate of Zinc.</i>						
Saturated solution,	1	3	18	0	19	0
1 part saturated solution,	1	0	8	0	19	18
1 part water,						
1 part saturated solution,	0	14	16	0	14	8
3 parts water,						
<i>Sulphuric Acid.</i>						
1 part to 8 of water,	3	1	6	1	4	8
1 part to 16 of water,	2	11	8	2	1	8
1 part to 24 of water,	2	7	3	2	5	6

HOW OFTEN SOLUTIONS SHOULD BE CHANGED AND ZINC AMALGAMATED.
 —Students have often put this question to us: How often should the solution in the cell be renewed, and the zinc plate be amalgamated? The following are the results of many trials made to ascertain the facts necessary to answer this inquiry. The zinc plates used were nearly 1 foot square, and the copper plate upon which the deposit was made was of the same size as the zinc plates.

In the first series the zinc plates were not taken out either to brush or re-amalgamate, neither were the solutions renewed during the time specified; but the zincs were newly amalgamated, and the solutions new at the commencement of each period.

		Copper deposited.		Zinc dissolved.	
		oz.	dwt.	oz.	dwt.
2 lbs common salt in one gallon of water,	24 hours, .	12	9	12	17
	48 hours, .	17	13	20	17
	60 hours, .	24	15	34	3
2 lbs. sulphate of zinc in one gallon of water,	24 hours, .	9	13	9	18
	48 hours, .	16	4	17	10
	60 hours, .	23	10	24	8
1 lb. sulphuric acid to 24 of water,	24 hours, .	15	17	17	15
	48 hours, .	27	16	32	3

From these results it is evident that the best and most economical manner would be to renew the solution every 24 hours; in the second 24 hours, as seen in the experiment of 48 hours with common salt, the extra deposit of copper is only 5 ounces 4 dwt., instead of 12 ounces 9 dwt. obtained in the first 24 hours; and the loss of zinc for this is 8 ounces instead of 5½, as it should be; and in the 60 hours the amount deposited is only equal to what will be got by two 24 hours with new solutions, and the loss of zinc is one-third more. With the sulphuric acid as the exciting solution, there is more work done in the 48 hours than is done by any of the other two exciting solutions in 60 hours; and even with the sulphuric acid it will be observed that the second 24 hours of the action is much less economical than the first. The difference in the cost of the exciting solutions is not worth consideration compared with the work done. To verify these results, our next series of experiments was with the same size of zinc and the same kind of solutions; but the zincs were taken out every 24 hours and brushed, but not re-amalgamated, and put back again with new solutions in the porous cell.

		Copper deposited.		Zinc dissolved.	
		oz.	dwt.	oz.	dwt.
Salt and water, .	4 days of 24 hours, .	49	16	51	8
Sulphate of zinc, .	4 days of 24 hours, .	47	14	48	9
Acid and water, .	3 days of 24 hours, .	48	13	53	7

These results give the most ample reply to the question so often put, and will guide the manufacturer as well as the student in his

operations, whether time or material be of the greatest consequence to him.

We may again remark that the sulphate of zinc solution does not require renewal; but when the zinc is brushed or re-amalgamated, half-empty the cell and refill it with water. The sulphate of zinc poured out being nearly saturated, may be crystallised, and may serve for other electro-metallurgical operations, or be sold.

Although these experiments were done with what is termed the single-cell system, our experience in depositing by a separate battery gave results still more in favour of the advantages obtained by keeping the zinc plates clean, and re-amalgamating them at short intervals, and also of the economical advantage of using dilute sulphuric acid with batteries that are in daily use, and where the object is *quantity* of metal deposited (see Description of Batteries).

MAKING OF MOULDS.—The directions given for obtaining a mould from a penny-piece by deposition, are applicable to taking moulds from any metallic medal, engraving, or figure that is not undercut, and for depositing copper within the moulds so produced. On the first discovery of this art, the electrotypist was confined to metallic moulds, as the deposition would not take place except upon metallic surfaces; but the discovery that plumbago, or blacklead polished, had a conducting power little inferior to that of metal, and that the deposit would take place upon its surface with nearly the same facility as upon metal, freed the art at once from many of its trammels, and enabled the operator to deposit upon any substance—wood, plaster of Paris, wax, &c.—by brushing the surface over with blacklead. It obliged the electro-metallurgist, however, to render himself expert in the art of moulding, since no good electrotype can be obtained without a perfect mould. We shall for this reason endeavour to give such instructions as will enable the student to make good moulds after a very short practice; but we need hardly add, that in this as well as in every operation, however plain may be the instructions and easy the manipulations, practice is necessary to ensure success; so that the student ought not to lose patience should his first attempt not succeed to his wishes. The substances used for taking moulds from objects to be copied by electrotype are bees'-wax, stearine, plaster of Paris, fusible metal, and gutta percha; indeed, any substance that will receive and retain an impression, and is not liable to be affected by the solution from which the metal is to be deposited, will serve the purpose. *The articles to be copied are generally composed either of*

plaster of Paris or metal. Suppose, in the first place, the article to be copied is of metal, and a mould is to be taken from it in wax or stearine. The latter we have not found to answer well alone; when used it should be mixed with wax, about half-and-half.

PREPARATION OF WAX.—Whether the bees'-wax have stearine in it or not, it is best to prepare it in the following manner:—Put some common virgin wax into an earthenware pot or pipkin, and place it over a slow fire; and when it is all melted, stir into it a little white-lead (flake white), say about one ounce of white lead to the pound of wax; this mixture tends to prevent the mould from cracking in the cooling, and from floating in the solution: the mixture should be re-melted two or three times before using it for the first time.

TO TAKE MOULDS IN WAX.—The medal to be copied should be brushed over with a little sweet oil; a soft brush, called a painters' sash tool, suits this purpose well: care must be taken to brush the oil well into all parts of the medal, after which the superfluous oil should be wiped off with a piece of cotton or cotton wool. If the medal has a bright polished surface, very little oil is required; but if the surface be *matted* or *dead*, it requires more care with the oil. A slip of cardboard or tin is now bound round the edge of the medal, the edge of which slip should rise about one-fourth of an inch higher than the highest part on the face of the medal: this done, hold the medal with its rim a little sloping, then pour the wax in the lowest portion, and gently bring it level, so that the melted wax may gradually flow over; this will prevent the formation of air-bubbles. Care must be taken not to pour the wax on too hot, as that is one great cause of failure in getting good moulds: it should be poured on just as it is beginning to set in the dish. As soon as the composition poured on the metal is *set* (becomes solid), undo the rim; for if it was allowed to remain on till the wax became perfectly cool, the wax would adhere to it, and being thus prevented from shrinking, which it always does a little, would be liable to crack. Put the medal and wax in a cool place, and in about an hour the two will separate easily. When they adhere, the cause is either that too little oil has been used, or that the wax was poured on too hot.

ROSIN WITH WAX.—Rosin has been recommended as a mixture with wax—mixtures of which, in various proportions, we have used with success; but when often used decomposition or some change

takes place, which makes the mixture granular and flexible, rendering it less useful for taking moulds. When rosin is used, the mixture, when first melted, should be boiled, or nearly so, and kept at that heat until effervescence ceases; it is then to be poured out upon a flat plate to cool, after which it may be used as described.

MOULDS IN PLASTER.—If a plaster of Paris mould is to be taken from the metallic medal, the preparation of the medal is the same as described above; and when so prepared with the rim of cardboard or tin, get a basin with as much water in it as will be sufficient to make a proper sized mould (a very little experience will enable the operator to know this), then take the finest plaster of Paris and sprinkle it into the water, stirring it till the mixture becomes of the consistence of thick cream; then pour a small portion upon the face of the medal, and with a brush similar to that used for oiling it gently brush the plaster into every part of the surface, which will prevent the formation of air bubbles; then pour on the remainder of the plaster till it rises to the edge of the rim: if the plaster is good, it will be ready for taking off in an hour. The mould is then to be placed before a fire, or in an oven, until quite dry, after which it is to be placed, back downwards, in a shallow vessel containing melted wax, not of sufficient depth to flow over the face of the mould, allowing the whole to remain over a slow fire, or upon a hot plate, until the wax has penetrated the plaster, and appears upon the face. Having removed it to a cool place to harden, it will soon be ready for electrotyping. If the mould is large and the plaster thick, the wax may be put upon the surface, and only as much as will penetrate a small way into the plaster. In both these instances the wax used is generally lost, and there is always liability of the copper solution passing through, and causing what is termed *surface deposit*, making the face of the medal rough. We may remark that although occasionally there may be a very good electrotype obtained from a plaster mould, still they are in general very inferior, as the saturating of the plaster has a tendency to blunt the impression, and the wax used for the purpose of saturation becomes expensive. It may be partially recovered by boiling the plaster in water: the wax melts out, and is obtained when the water cools. Plaster should not be used for moulds where wax can be employed, being neither so good nor so economical; but there are cases in which the moulds being very large, the use of plaster is unavoidable.

MOULDS IN FUSIBLE ALLOY.—This name is given to alloys of two or more metals which melt at very low temperatures ; it suits the purpose of taking moulds of small objects very well. The following are examples of such compositions :—

Tin.	Lead.	Bismuth.
1	1	2
3	2	5
1	2	3
3	5	8

These all melt at a temperature below that of boiling water; the ingredients are melted together in an iron ladle, poured out upon a flat stone, broken up, and re-melted in the same way two or three times, in order that they may be thoroughly mixed. The medal from which the mould is to be taken is prepared in the same manner as described for wax.

The means of taking moulds with fusible metal are the following:—The fusible alloy is melted and poured into a saucer, or, what does better, a small wooden tray; the operator now watches it till it cools down into a semi-fluid state, or to the point of setting, when he brings the medal suddenly upon it, face downwards, and holds it there until the alloy has fairly set; he then allows it to cool, and undoes the slip around the medal, from which the mould will easily separate. The height of the slip of paper above the surface of the medal determines of course the thickness of the mould. The beginner very seldom succeeds in his first attempts at making moulds in fusible alloy; but as a little experience teaches more than the reading of an essay upon the subject, he will soon find both his patience and labour rewarded with gratifying success. Or the melted alloy may be poured upon the face of the medal in the same manner as described for taking wax moulds; but this method does not do so well: however, as these alloys all melt at the heat of boiling water, the medal or object being moulded may be kept at a temperature that will keep the alloy melted either by placing them into a water-bath or oven; after being kept in the melted state over the medal for a few minutes they are removed and allowed to cool, when the mould and medal are easily separated. Some of the finest moulds are taken by this process; but from the constant loss of the materials by oxidation, &c., it is expensive, so that the use of such alloys amongst electro-metallurgists is very limited.

MOULDS IN GUTTA PERCHA.—Gutta percha, as a material for moulding, serves the purpose most admirably. We have seen moulds of this

substance equal, if not superior, to any that we ever saw taken in wax, and of a depth of cutting which it would have been very difficult to have taken in wax. The method adopted for taking moulds is to heat the gutta percha in boiling water, or in a chamber heated to the temperature of boiling water, which makes it soft and pliable. The medal is fitted with a metallic rim, or placed in the bottom of a metal saucer with a cylindrical rim, a little larger than the medal; the medal being placed back down, a quantity of gutta percha is pressed into the saucer, and as much added as will cause it to stand above the edge of the rim: it is now placed in a common copying press, and kept under pressure until it is quite cold and hard. The impressions taken in this way are generally very fine; when the medal is not deep cut, a less pressure may suffice, but when the pressure is too little the impression will be blunt.

Stereotypes and engraved plates of large size and fine patterns are copied in this way by the electrotype process. The Bank of France in order to prevent counterfeiting their notes, has upon the same plate all kinds of engraving done by different artists, whose work can be recognised, and this plate is copied by taking a gutta percha mould in the manner described, and depositing copper upon it. Gutta percha may be softened by mixing with it a small quantity of oil, tallow, or wax. Gutta percha takes a coating of blacklead readily, and the deposit goes over it easily.

A mixture of gutta percha and marine glue has been recommended for moulds as superior to gutta percha alone. We have not found this recommendation to be of general utility; when moulds are small, and used immediately after being made, they do very well; but when of large size, and allowed to stand for any length of time, they have a tendency to lose their shape and even their proportions.

MOULDS FROM FERNS, SEAWEED, &c.—A method of taking impressions of fern leaves and seaweeds was proposed by Dr. F. Branson, in the *Athenæum*. It is thus described:—

“A piece of gutta percha, free from blemish, and the size of the plate required, is placed in boiling water. When thoroughly softened, it is taken out and laid flat upon a smooth metal plate, and immediately dusted over with the finest bronze powder used for printing gold letters. The object of this is threefold—to dry the surface, to render the surface more smooth, and to prevent adhesion. The plant is then to be neatly laid out upon the bronze surface, and covered with a polished metal plate either of copper or of German silver. The whole is then to be

subjected to an amount of pressure sufficient to imbed the upper plate in the gutta percha. When the gutta percha is cold, the metal plate may be removed and the fern gently withdrawn from its bed. A beautiful impression of the fern will remain." If the bronze powder adhering to the gutta-percha mould is not sufficient to act as a conductor for receiving the deposit, this property can be ensured by brushing over the surface of the mould with fine blacklead, when a perfect electrotype copy of the fern can be obtained.

We have seen many electrotype leaves done by this method, which were certainly very pretty as electrotypes, and the process is well adapted for flat leaves; but the pressure required renders it unsuitable for many kinds of leaves, indeed it destroys the natural forms of the greater number both of leaves and seaweeds. The products of the process cannot, indeed, be compared with those electrotype leaves the moulds of which are taken by wax. The great merit of the process is its ease and simplicity. The method given for taking the mould of the leaf is suitable for any kind of flat mould in gutta percha. The mould of a leaf may be taken in plaster, by placing the leaf upon dry sand and pressing the sand under and on each side to fill up the spaces under the leaf, so as to bear the pressure of the plaster, putting a collar of paper round the sand to prevent its yielding, and then pouring the plaster over the whole. When the plaster is set, the leaf is removed and the plaster trimmed round with a knife. This also has its difficulties; for when leaves have hairs upon them, they stick into the plaster. The method of taking moulds of leaves in wax is by holding the leaf in the hand, and brushing a thin layer of melted wax over the surface to be moulded, allowing this to harden, and then brushing on another layer, and so on until the wax is sufficiently thick to suffer handling. The leaf is then gently drawn off the wax, which is to be blackleaded, and put into the electrotype apparatus to receive the coating of copper. A type of the leaf is by this means obtained with all its natural convolutions.

NATURE PRINTING.—Another method for making moulds of leaves and other vegetable objects has been practised by an eminent firm in London. The leaf is carefully dried and laid upon a smooth piece of milled lead, which is placed between two steel plates, and passed between rollers; these press the leaf into the lead, and produce a complete mould. Copies from this may be taken with gutta percha or electrotype. Printed impressions of leaves, seaweed, and such like objects prepared in this way, may be seen in an excellent work pub-

lished by Bradbury and Evans; and a full detail of the process, with specimens, will be found in the *Proceedings of the Royal Institution* for 1854. The same objections apply to this process as to that by the gutta percha. Roseleur describes the copying of nettle and other leaves so perfect that all the hairs on their surface were to be seen thus,—“One of the sides of a fresh leaf was covered by means of a brush with a thin paste of plaster of Paris, and after the drying of this first coat, other layers were applied, until a resisting block had been obtained with the leaf uppermost. The free side was then covered with several coats (always with a brush or pencil) of gutta percha dissolved in bisulphide of carbon, and lastly with melted gutta. The mould was removed from the leaf, metallised, and immersed in the galvano-plastic bath.”

CASTING OF REPTILES, &c.—Imbed the subject in a mould made of four parts of plaster of Paris, one of unburnt lime powder, and one of Flanders brick-dust. Dry the mould carefully in an oven, then make it red-hot, and burn the subject out of it, taking care to free the mould from the ashes. Before putting this mould into the oven to dry, insert two or more iron or smooth wooden pins, one end touching the object inside, the other projecting outside. When the mould is dried, and before burning, these are carefully removed to allow escape of gas and to remove the ashes; by a proper arrangement of these holes the carbon of the article may be consumed, when the remaining ash is easily removed. Fusible metal may be cast in this mould, or a wax model may be taken of the object, pouring the wax in just before setting. The whole is now placed in water, the lime causes the mould to dissolve or break up, and the figure modelled within it may be taken and covered with copper, and the wax afterwards melted out. Flowers, insects, lizards, and other little animals may be typed in this way. In all these processes, perseverance and care are the best cures for little difficulties.

WAX MOULDS FROM PLASTER.—If the object, which we assume to be a medal, from which the mould is to be taken, be composed of plaster of Paris, and the mould to be taken in wax, the first operation is to prepare the plaster medal. Some boiled linseed-oil, such as is used by house-painters, is to be laid over the surface of the medal with a camel's hair pencil, and continued until it is perfectly saturated, which is known by the plaster ceasing to absorb any more of the oil. This operation succeeds best when the medal is heated a little. The medal should now be laid aside till the oil completely dries, when the plaster will be found to be quite hard, and having the appearance of polished marble;

it is consequently fit to be used for taking the wax mould, which is done in the same manner as we have described for taking a wax mould from a metallic metal.

Many prefer saturating the medal with water: this is best done by placing the medal back down in the water, but not allowing it to flow over the face; the water rises by capillary attraction to the surface of the medal, rendering the face damp without being wet. The rim being now tied on the plaster medal, the melted wax is poured upon it. This method is equally good, but liability to failure is much greater, caused generally by the wax being too hot.

The plaster medal may also be saturated with skimmed milk, and then dried; by repeating this twice, the plaster assumes on the surface an appearance like marble, and may be used for taking wax moulds.

MOULD OF PLASTER FROM PLASTER MODELS.—When a plaster mould is to be taken, the face of the model is prepared differently to that described, in order to prevent the adhesion of the two plasters. The best substance we have tried for this purpose is a mixture of soft soap and tallow, universally used by potters for preparing their moulds, and called by them *lacquer*. It is prepared in the following manner:—Half-a-pound of soft soap is put into three pints of clean water, in any convenient vessel, which is set on a clear fire, and the solution kept in agitation by stirring; when the mixture begins to boil, add from one ounce to an ounce and a half of tallow, and keep boiling till it is reduced in bulk to about two pints, when it is ready for use. The surface of the medal must be washed over with this lacquer, allowing it to absorb as much as it can, when it assumes the appearance of polished marble; it is now prepared with a rim of paper, and the mould taken as directed for taking plaster moulds from metallic medals. When hardened, they will separate easily. Wetting the plaster model with a solution of soap before taking the cast will do, or, if the plaster model has been saturated with oil or milk, it has only to be moistened with sweet oil, the same as a metal model.

FUSIBLE ALLOY FROM PLASTER.—If a mould of fusible metal be required from a plaster medal, the plaster may be saturated either with boiled oil or the soap and tallow lacquer, and the mould taken in the same manner as from a metallic medal.

COPPER MOULDS FROM PLASTER.—Many electro-metallurgists prefer taking a mould in copper when the medal is of plaster of Paris. This

is done by the electrotype process : the plaster model is saturated with wax over a slow fire, as already detailed, and then prepared for taking an electrotype in the usual manner (see page 56). We need hardly mention that the model in this case is destroyed ; but notwithstanding, in the case of plaster models, to take a copper mould is the most preferable way, as it may be repaired in case of slight defect, and it may be used over and over again without deterioration.

When an electrotype is required of a model that is undercut, or of a bust or figure, the process which we have described will not answer, as the mould cannot separate from the model. In such circumstances, the general method of proceeding is to cast the mould in separate pieces, and then join these together. The material used for this purpose is plaster of Paris ; the operation, however, to be done well, requires a person of considerable experience. If the undercutting is not very great, a gutta percha mould can be taken by the process already described ; but before removing the mould subject it to a heat of boiling water to soften the gutta, which by careful manipulation may be removed without damage to either mould or model.

ELASTIC MOULDING.—The process patented by Mr. Parkes for taking a mould of any kind of model in one piece, is excellently adapted for the electrotypist. The material is composed of glue and treacle : 12 lbs. of glue is steeped for several hours in as much water as will moisten it thoroughly. This is put into a metallic vessel, which is placed in boiling water, as a hot bath. When the glue falls into a fluid state, 3 lbs. of treacle are added, and the whole is well mixed by stirring. Suppose now that the mould of a small bust is wanted, a cylindrical vessel is chosen, so deep that the bust may stand in it an inch or so under the edge. The inside of this vessel is oiled, a piece of stout paper is pasted on the bottom of the bust, to prevent the fluid mixture from going inside ; and if it is composed of plaster, sand is put inside to prevent it from swimming. It is next completely drenched in oil, and placed upright in the vessel ; this done, the melted mixture of glue and treacle is poured in till the bust is covered to the depth of an inch. The whole must stand for at least twenty-four hours, till it is perfectly cool throughout ; after which it is taken out by inverting the vessel upon a table, when, of course, the bottom of the bust is presented bare. The mould is now cut by means of a sharp knife, from the bottom up the back of the bust to the front of the head. It is next held open by the operator, when an assistant

lifts out the bust, and the mould is allowed to reclose; a piece of brown paper is tied round it to keep it firm. The operator has now a complete mould of the bust in one piece; but he cannot treat it like wax moulds, as its substance is soluble in water, and would be destroyed if put into the solution. A mixture of wax and rosin, with occasionally a little suet, is melted, and allowed to stand till it is on the point of setting, when it is poured carefully into the mould, and left to cool. The mould is then untied and opened up as before; the wax bust is taken out, and the mould may be tied up for other casts. Besides wax and rosin, there are several other mixtures used—deer's fat is preferable to common suet, stearine, &c. The object is to get a mixture that takes a good cast, and becomes solid at a heat less than that which would melt the mould.

MOULDING OF FIGURES.—If the model or figure be composed of plaster of Paris, a mould is often taken in copper by deposition: the figure is saturated with wax, as described for a medal, and copper deposited upon it sufficiently thick to bear handling, without damage when taken from the model. The figure with the copper deposit is carefully sawn in two, and then boiled in water, by which the plaster is softened and easily separated from the copper, which now serves as the mould in which the deposit is to be made. It is prepared in the same way as we have described for depositing in copper moulds. When the deposit is made sufficiently thick, the copper mould is peeled off, and the two halves of the figure soldered together. The copper moulds which are deposited upon the wax models taken in the elastic moulding are often treated in the same manner; but more generally these moulds are used for depositing silver or gold into them, to obtain *fac-similes* of the object in these metals, in which case the copper moulds are dissolved off by acids, as will be described in a subsequent section.

FIGURES COVERED WITH COPPER.—When plaster busts or figures are wanted in copper, the most usual way is to prepare the figure with wax as described, and to coat it over with a thin deposit of copper, letting the copper remain. Some operators, when it can be done, remove the plaster, and wash over the inside with an alloy of tin and lead melted. In this case the copper must previously be cleaned by washing first in a solution of potash, and then with chloride of zinc: the latter mode will cause the alloy to adhere to the copper, and give it strength. In either of these cases the deposit must not be very

thick, or it will throw the figures out of proportion, such as the features of a bust, &c. Any slight roughness of deposit may be easily smoothed down by means of fine emery.

THE PREPARATION OF NON-METALLIC MOULDS TO RECEIVE DEPOSIT.—Having detailed what we have found best for obtaining moulds of objects for the purpose of electrotyping, we proceed to the manner of obtaining a deposit upon these moulds. Were any of the plaster or wax moulds attached to the zinc, and immersed in the copper solution, no deposit would be obtained, because neither the plaster nor the wax is a conductor of electricity. Some substance must now be applied to the surface, in order to give it conducting power. There are several ways of communicating this property, to be afterwards described; but the best and most simple for the articles under consideration is to apply common blacklead (already referred to) in the following manner:—A copper wire is put round the edge of the medal, or if wax moulds are used, a thin slip of copper may be inserted into the edge of the mould, or being slightly heated and laid upon the back, the two will adhere. A fine brush is now taken (we have found a small hat-brush very suitable) and dipped into fine blacklead, and brushed over the surface of the medal; the brushing is to be continued until all the face round to the wire upon the edge, or slip of copper forming connection, has a complete metallic lustre; a bright polish is necessary to the obtaining a quick and good deposit.

In brushing on the blacklead, care should be taken not to allow any to go upon the back or beyond the copper connection, or the deposit will follow it, and so cause a loss of copper, and make the mould more difficult to separate from the deposit—being, as it were, incased. If the electrotypist takes the labour himself of filing off all the superfluous copper from the edge of his deposited medal, it will do more than any written precautions to teach the necessity of preventing as much as possible the deposit going farther than is necessary. When the face of the mould is properly blackleaded, the copper wire connected with it is attached to the zinc plate in the porous cell, and the mould immersed in the copper solution: as shewn in Fig. 29 the deposit will immediately begin upon the copper connection, and will soon spread over every part, covering the blacklead polish with less or more facility, according to the state of the solutions and other circumstances to be afterwards noticed. When the deposit is considered sufficiently thick for removing—which, in ordinary circum-

stances, will require from two to three days—the medal is taken out of the solution, and washed in cold water, and the connection is taken off. If the deposit has not gone far over the edge of the mould, the two may be separated by a gentle pull; if otherwise, the superfluous deposit must be eased off, and if care be taken the wax may be fit to use over again; but when the mould is plaster of Paris, however well it may be saturated with wax or other substance, it is seldom in a condition to use again. If the plaster mould be large and thick, it is advisable to coat the back with wax or tallow, which is done by brushing it over with either substance in a melted state: the mould being cold it will not absorb the wax or tallow, hence it may be recovered again (see page 63). The sulphate of copper possesses so penetrating a quality that if the slightest imperfection occurs in the saturation of the mould by wax, or if imperfectly protected, the solution will penetrate through it, and the copper will be deposited upon the face of the object adhering to the plaster, giving to the medal a rough, matted appearance, and seriously injuring it.

USING METAL MOULDS.—A mould in fusible alloy does not require to be blacklead, but the back and edge must be protected by a coating of wax or other non-conducting material; it may be connected in the same way as the penny-piece (page 56), by putting a wire round its edge previous to laying on the non-conducting substance, such as tallow or wax, which should also cover the wire. Or a slip of copper or wire may be laid upon the back and fastened by a drop or two of sealing-wax; the back is then coated, but care must be taken that the wax does not get between the connection and the medal, which will prevent deposit. The deposit on this mould goes on instantaneously, the same as over the penny-piece. When sufficiently thick, it may be taken off in the same manner as from the wax mould, the surface having been prepared by turpentine (page 56) to prevent adherence. These moulds may be used several times, if care be taken not to heat them to the melting point.

The medals obtained from metallic moulds prepared with the turpentine solution, have a bright surface, which is not liable to change easily; but if the mould has been prepared with oil or composed of wax or plaster, the metal will either be dark, or will very easily tarnish. The means of preserving them, either by bronzing or plating with other metals, will be detailed in a subsequent section.

PRECAUTIONS ON PUTTING THE MOULDS INTO A SOLUTION.—In put-

ting moulds into the copper solution, the operator is often annoyed by small globules of air adhering to the surface, which either prevent the deposit taking place upon these parts, or, when they are very minute, permit the deposit to grow over them—causing small hollows in the mould, which give a very ugly appearance to the face of the medal. To obviate this, give the mould, when newly put into the solution, two or three shakes, or give the wire attached to it, while the mould is in the solution, a smart tap with a key or knife, or anything convenient; but the most certain means we have tried is to moisten the surface with alcohol just previous to putting it into the copper solution. A little practice in these manipulations will soon enable the student to avoid these annoyances.

DEPOSITION ON LARGE OBJECTS.—When busts or figures, whether of wax or plaster of Paris, are to be coated with copper, with no other conducting surface than blacklead, it is attended with considerable difficulty to the inexperienced electrotypist. The deposit grows over all the prominent parts, leaving hollow places, such as armpits, neck, &c., without any deposit; and when once missed, it requires considerable management to get these parts coated, as the coated parts give a sufficient passage for the current of electricity. It is recommended by some electrotypists to take out the bust, and coat the parts deposited upon with wax, to prevent any further deposit on them; but this practice is not good, especially with plaster of Paris, for an electrotype ought never to be taken out till finished. Sometimes the resistance of the hollow parts is occasioned by the solution becoming exhausted of metal from its position in regard to the positive pole. In this case a change of position effects a remedy. It may be remarked, that when a bust or any large surface having hollow parts upon it, is to be electrotyped, as many copper connections as possible ought to be made between these parts and the zinc of the battery. Let the connections with the hollow parts be made with the finest wire which can be had, and let the zinc plate in the cell have a large surface compared to the surface of the figure, and the battery be of considerable intensity; if attention is paid to these conditions, the most intricate figures and busts may be covered over in a few hours. Care has to be observed in taking off the connections from the deposit, or the operator may tear off a portion of the deposit: if the wires used are fine, they should be cut off close to the deposited surface.

TO MAKE BUSTS AND FIGURES.—Busts and figures, and other com-

plicated works of art, which cannot be perfectly coated with blacklead, may be covered by a film of silver or gold, which serves as a conducting medium to the copper. This is effected by a solution of phosphorus in bisulphide of carbon. The operation being patented, we will take advantage of the description given of it in the specification. "The solution of phosphorus is prepared by adding to each pound of that substance 15 lbs. of the bisulphuret or other sulphuret of carbon, and then thoroughly agitating the mixture; this solution is applicable to various uses, and amongst others, to obtaining deposits of metal upon non-metallic substances, either by combining it with the substances on which it is to be deposited, as in the case of wax, or by coating the surface thereof. Any of the known preparations of wax may be treated in this way, but the one preferred is composed of from 6 to 8 ounces of the solution: 5 lbs. of wax and 5 lbs. of deer's fat, melted together at a low heat, on account of the inflammable nature of the phosphorus. The article formed by this composition is acted upon by a solution of silver or gold, in the manner hereinafter described with respect to articles which have been coated with the solution."

Roseleur states that, "When plumbago is moistened with a solution of chloride of gold in ether, and then allowed to dry in a shallow vessel exposed to solar light, we obtain gilt *plumbago*, which is much more conducting than plumbago alone. We also manufacture a *silvered plumbago* by calcining, at a red heat and in a closed crucible, a plumbago which has been moistened with an aqueous or ammoniacal solution of 50 to 100 grammes of nitrate of silver per kilogramme of graphite employed."

COATING OF FLOWERS, &c.—"If the solution is to be applied to the surface of the article, an addition is made to it of one pound of wax or tallow, one pint of spirits of turpentine, and two ounces of India rubber, dissolved with one pound of asphalt, in bisulphide of carbon, for every pound of phosphorus contained in the solution. The wax and tallow being first melted, the solution of India-rubber and asphalt is stirred in; then the turpentine, and after that the solution of phosphorus is added. The solution prepared in this manner is applied to the surfaces of non-metallic substances, such as wood, flowers, &c., by immersion or brushing: the article is then immersed in a dilute solution of nitrate of silver, or chloride of gold; in a few minutes the surface is covered with a fine film of metal, sufficient to insure a deposit of any required thickness on the article being connected with any of the electrical apparatuses at present employed for coating articles with metal. The

solution intended to be used is prepared by dissolving four ounces of silver in nitric acid, and afterwards diluting the same with twelve gallons of water; the gold solution is formed by dissolving one ounce of gold in nitro-muriatic acid, and then diluting it with ten gallons of water."

We have frequently repeated the operations described by this patentee with entire satisfaction, and were enabled to cover every variety of surface with great facility.

The solutions of silver and gold, prepared as above, will last for a long time, and do a great many articles. When it is convenient it is best to use both solutions. The connecting wire should first be attached to the article to be coated, before being dipped into the phosphorus solution, but connected at such parts as will not hurt the appearance of the object by leaving a mark when it is taken off. Care should be taken not to touch the article with the hands after it is dipped into the solution. The object supported by the connections is immersed in the phosphorus solution, where it remains for two or three minutes. When taken out it is dipped into the silver solution, and as soon as the surface becomes black, having the appearance of a piece of black china, it is to be dipped several times in distilled water, and then immersed in the solution of protochloride of gold about three minutes: the surface takes a bronze tinge by the reduction of the gold. It is next washed in distilled water by merely dipping, not by throwing water upon it. The wire connection is now attached to the zinc terminal of a battery, and then the article put into the copper solution, and in a few minutes the article is coated over with a deposit of copper. A thin copper surface may thus be given to small busts or figures without sensibly distorting the features by want of proportion.

FIGURES FROM ELASTIC MOULDS.—When taking a wax cast from the elastic mould, described in page 69, after taking out the mould it is only necessary to make the connections, and pass it through the gold and silver solutions, as described, and then to connect it with the battery.

We may also mention that the principal object of making copper moulds by this process, in the manufactory, is not to make *fac-similes* in copper, but to make articles of solid silver or gold. Copies of highly wrought work, either chased or engraved, or of articles, duplicates of which cannot be obtained, or of which the workmanship is costly, may by this means be made in solid silver or gold, at little more expense than the cost of the metal. Having obtained the copper mould, silver is

deposited in it to any thickness, and the copper dissolved off. However, an extensive trade is now being carried on in figures and other works of art deposited in copper and then bronzed, which gives them an appearance often not much inferior to that of antique works of the highest art. There are also some beautiful ornamental works got up by manufacturers. Small figures and other highly wrought ornaments are made by the electrotype process, and then soldered upon a plain vessel made of copper or German silver—such, for example, as a biscuit box—the whole is then plated, or gilt with gold or silver, producing a rich ornamental article of great beauty at a comparative trifling cost.

ELECTROTYPES FROM DAGUERREOTYPES.—What may be justly termed the perfection of electrotyping is the production of electrotypes from daguerreotypes. The daguerreotype picture being taken, a small portion of the back is cleaned with sandpaper, taking care not to allow anything to touch the face; a little fine solder is placed on this part; a piece of flattened wire, also cleaned, is placed upon the solder, the whole moistened with dilute muriatic acid, or chloride of zinc. The wire is now held over the gas or a lamp, about half an inch from the plate; the heat is transmitted through the wire to the solder, which melts, and the wire is soldered to the type; the back is then protected by wax, and the daguerreotype is put into the copper solution in the same manner as a medal; the deposit proceeds rapidly, and when sufficiently thick the two easily separate, and an impression of the picture is obtained from the daguerreotype with an expression softer and finer than the original: several electrotypes may, with care, be taken from one picture. The electrotype may now be passed through a weak solution of cyanide of gold and potassium, in connection with a small battery, and thus a beautiful golden tint be given to the picture, which serves to protect it from the action of the atmosphere; but they should also be protected by glass, which may be fixed on in the manner pointed out in another section. The most successful operators that we have known in this and several other departments of electrotyping were the late Dr. Thomas Paterson, of Glasgow, and Mr. Bawtree, of London.

DEPOSITING BY SEPARATE BATTERY.—Having described, so far as we know them, the best and most simple means of obtaining moulds, and their preparation for receiving the deposit of the metal, we return again to the management of solutions and batteries, and the application to other metals besides copper.

Although in our account of the porous or single cell system (page

56) we have recommended it as the best and most economical for electrotyping medals and other small articles, still many eminent electro-metallurgists prefer using the battery system; and, indeed, there are solutions of copper and of other metals to which the porous cell system cannot be applied, from the nature of the solution and the necessity of intensity to decompose them. Besides, the separate battery process is attended with much less trouble, as the copper solution is not liable to exhaustion. We have already referred to Mason's improvement, page 21, as suggesting the use of a separate battery. At the risk of a little repetition, we will again draw the reader's attention to the principles of it.

While depositing upon a mould by the single cell, if the wire which connects them be cut in the middle, and a mould be attached to the end of the portion remaining upon the zinc plate, and a small plate of copper to the end of the wire remaining upon the mould in the copper solution, and let these two be put into a second vessel containing a solution of sulphate of copper, the action between the zinc and medal in the first pair will go on as before—namely, the electricity passing from the zinc through the porous cell and the solution to the medal is made to pass through the copper solution, which is in the second vessel, between the mould and copper plate, where it produces the same effects as in the first cell. The sulphuric acid is liberated at the copper plate and dissolves it, and the copper is deposited upon the mould, so that the solution in this cell is maintained at one strength: hence there is no necessity for hanging crystals of sulphate of copper in this solution. (See Fig. 31.)

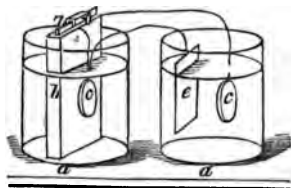


Fig. 31.

It will be observed, that the electricity having to pass through a second solution, is made to perform double duty, and must consequently be much more economical. We found the results to be these:—A single cell, with a mould, was placed two inches from the porous cell, and of the same size as the zinc plate, and another, similarly arranged, but connected with a metal mould and copper plate of similar size to the zinc and copper, was placed one inch apart in the copper solution of second cell, when the mould in the single cell had gained 100 grains and the zinc plate lost 108 grains. The mould in the battery cell of the other arrangement had only deposited upon it 30 grains, the zinc plate had lost 35 grains; but the mould in the second or decomposition cell had also deposited upon it 30 grains, making in all 60 grains deposited,

for 35 zinc dissolved, but requiring for this nearly double the time. These arrangements, as we have before observed, are simply a single pair of Daniell's battery connected with a decomposition cell; these

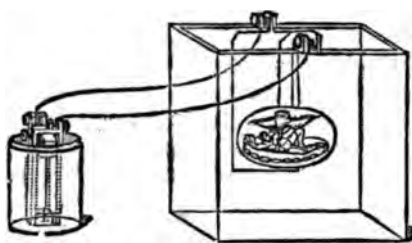


Fig. 32.

advantages are not applicable to any other battery, as in no other battery does deposition take place within the battery cells; indeed, this method of using a compound depositing apparatus is very seldom employed.

Batteries of a different form from Daniell's, and used apart from the decom-

position cell, where the medal is being formed, are generally adopted. Fig. 32 represents a Smee's battery, connected with a medal and copper

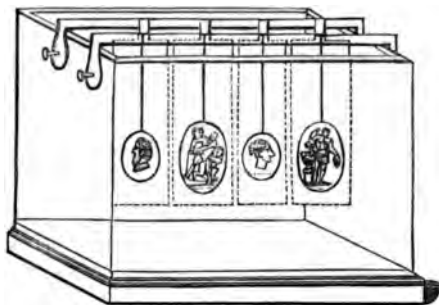


Fig. 33.

plate in a separate cell; and Fig. 33 is a large decomposition trough for doing several medals at one time: of course any battery may be attached to these medals and plate by the brass connections seen on the end of the trough—bearing in remembrance, that the zinc of the battery is connected with

the medals, and the copper or platinised silver with the copper in the decomposition cell. (See Different Forms of Batteries).

SIZE OF THE ELECTRODES.—When a separate battery is used for the purpose of depositing in a decomposition cell, there are several conditions which are well to be observed, as they influence the amount and character of the deposit. The first is the size of the electrodes or medals, in relation to size of the zinc in the battery. The results we have obtained, in working with an ordinary zinc and copper battery, excited by dilute sulphuric acid, the size of the zinc plates immersed in the acid being 8 inches square = to 128 square inches, both sides of the zinc being utilised, may be expressed in general terms; thus, when

the deposit upon the electrodes of the same size as the zinc plates in the battery equalled 100, that upon electrodes one half the size of the zinc plates in the battery equalled 57, and upon electrodes double the size of the zincs of the battery 190; but these conditions are affected by the intensity of the arrangement and the nature of the solution in the decomposing cell. These experiments were with a common zinc and copper battery, of the form given at page 37—the electrolyte being sulphate of copper, in what is called good working condition.

RELATIVE POWER OF BATTERIES.—The following experiments, made with electrodes double the size of the zinc plates of the batteries, all at equal distances (1 inch apart), will shew the relative power of the batteries used. The time in action was one hour each: only one pair of plates constituted the battery: size of plates 4×6 inches.

Grove's battery deposited	. . .	104 grains.
Single cell,	62 „
Daniell's,	33 „
Smee's,	22 „
Wollaston's,	18 „

CONSTANCY OF BATTERIES.—The first hour of the action of most batteries differs from that time afterwards, so that one kind of battery may be most useful for a short time, and another sort if the action is to be continued for a length of time. The following table will illustrate this remark, the condition being the same as in last experiment, or the last experiments being continued, and the results taken every hour for seven successive hours :—

	1 hour.	2 hours.	3 hours.	4 hours.	5 hours.	6 hours.	7 hours.	Total.
Grove's battery, .	104	86	66	60	54	49	45	464 grs.
Single cell, . .	62	57	54	46	39	29	24	311 „
Daniell's, . . .	33	35	34	32	32	30	31	227 „
Smee's,	22	16	14	11	12	11	10	96 „
Wollaston's, . .	18	14	15	12	11	10	10	90 „

To make this comparison more practical, larger plates were used for the batteries, but all of equal size and proportionately larger electrodes, and the batteries kept in operation until one pound of copper was

deposited, renewing the acid and brushing the zincs every 24 hours. The time taken to effect this was—

Grove's battery,	19½ hours.
Single cell,	45 „
Daniell's,	49 „
Smee's,	147 „
Wollaston's,	151 „

The Daniell's battery used in this experiment had flat plates, not circular, as described at page 41. We may also remind the reader that a single cell is a Daniell, but as thus used is more effective, by having less resistance.

COMPARATIVE PRODUCE OF BATTERIES.—The expense of the materials used in these experiments was as follows (of course the materials will differ in cost both at different times and in different localities, and more common materials may be used):—

By the process with Grove's battery, one pound of deposited copper costs—

	s.	d.
1 lb. Copper, from positive electrode,	1	0
1¼ lb. Amalgamated zinc,	0	10
1½ lb. Nitric acid,	0	9
Sulphuric acid,	0	1
	2	8
Add time, say halfpenny per hour, for comparison,	0	9½
	3	5½

By single cell apparatus, one pound of deposited copper costs—

	s.	d.
1 lb. Sulphuric acid,	0	2
1⅞ lb. Amalgamated zinc,	0	8½
4 lbs. Sulphate of copper,	1	6
	2	4½
Time, at halfpenny per hour,	1	10½
	4	3

By Daniell's battery, one pound of deposited copper costs—

	<i>s.</i>	<i>d.</i>
$1\frac{3}{8}$ lb. Amalgamated zinc,	0	9
4 lbs. Sulphate of copper,	1	6
1 lb. Copper from electrode,	1	0
Sulphuric acid,	0	1
	<hr/>	
	3	4
Time, at halfpenny per hour,	2	$0\frac{1}{2}$
	<hr/>	
	5	$4\frac{1}{2}$

By Smee's battery, one pound of deposited copper costs—

	<i>s.</i>	<i>d.</i>
$1\frac{1}{2}$ lb. Amalgamated zinc,	0	10
3 lbs. Sulphuric acid,	0	6
1 lb. Copper from electrode,	1	0
	<hr/>	
	2	4
Time, at halfpenny per hour,	6	$1\frac{1}{2}$
	<hr/>	
	8	$5\frac{1}{2}$

By Wollaston's battery, one pound of deposited copper costs—

	<i>s.</i>	<i>d.</i>
1 lb. Copper from electrode,	1	0
$1\frac{3}{8}$ lb. Amalgamated zinc,	0	9
3 lbs. Sulphuric acid,	0	6
	<hr/>	
	2	3
Time, at halfpenny per hour,	6	$3\frac{1}{2}$
	<hr/>	
	8	$6\frac{1}{2}$

By thus adding the time, at a given rate, it serves to illustrate what we have before stated respecting the necessity of placing the value of time against the cost of materials. In manufactories where time, rent, capital, &c., have to be paid for, it may be cheapest to use the battery with the most costly materials; but where time is of no consideration, or, as is often the case, if, while the operations are going on, the workmen are employed in other necessary labour, a cheaper apparatus will answer; but the student or manufacturer will, by the above general results, be enabled to choose the process most suitable for his purposes. It must be borne in mind that an allowance has to be made on the first, second, and third, for wear and tear of porous vessels, not included in

the above estimate. Although the results of these experiments give, exclusive of time, the cost of one pound of electrotyped copper, thus—

	s.	d.
Grove's battery,	2	8
Single cell,	2	4½
Daniell's,	3	4
Smee's,	2	4
Wollaston's,	2	3

still we know from long experience in the use of single cell, Smee's, and Wollaston's batteries, for manufacturing purposes, that the price of the pound of copper deposited may be more correctly stated at 2s. 6d.—there being always loss in making the purest article (the copper) from impure materials, as the sulphate of copper, or the ordinary copper of commerce, which is used as electrodes. Every electrotypist will not fail to observe that the copper positive electrode in the depositing cell soon gets dark in colour, and covered with a thin film of black slimy matter, which causes a certain loss. An analysis of a sample of this matter is given by Max, Duke of Leuchtenberg, in the *Progress of General Science*, vol. ii., as follows:—

Sand,	1.90
Antimony,	9.22
Tin,	33.50
Arsenic,	7.40
Platinum,	0.44
Gold,	0.98
Silver,	4.45
Lead,	0.15
Copper,	9.24
Iron,	0.30
Nickel,	2.26
Cobalt,	0.86
Vanadium,	0.64
Sulphur,	2.46
Selenium,	1.27
Oxygen,	24.82

An analysis of this sort invests the subject with great interest. We wish there had also been given an analysis of the solution in which the electrode was placed, as well as the copper that was used as the electrode,

and the quantity of black matter obtained, and the quantity of copper dissolved to yield that product: for the analysis indicates an amount and diversity of impurities in copper that has never hitherto been thought of. However, it is a known fact, that the more impure the copper is that is used for a pole, the black matter is not only more easily but more abundantly produced.

Mr. Smee, in his "Advice to capitalists who propose entering upon the business of electro-metallurgy," gives a table of expenses incurred by the use of different batteries. But his rules are based too exclusively upon theoretical considerations, and without that regard for practical conditions which are so important to the manufacturer. Mr. Smee recommends for use what he calls "an odds-and-ends battery," composed of odd scraps of zinc put into acid, having in the same vessel a piece of copper or platinised silver, and a wire placed in contact with them which forms the electrode. This battery may be convenient for the amateur electrotypist, as it enables him to use up all his waste zinc. Raw zinc or spelter, Mr. Smee says, may also be used in this way, constituting the cheapest of all batteries for manufacturing purposes. The data of his calculations are as follows:—The copper sheet forming the positive electrode is quoted at 1s. per lb.; wrought zinc, 7d. per lb.; raw zinc at a little more than half the price of wrought zinc, which we will call 4d. per lb., although he rates it at 5d. Iron is given at from 1d. to 2d. per lb. The equivalent weight of copper is given at 32, of zinc at 32, and of iron at 28; that is to say, 32 parts (say ounces) of zinc dissolved in the battery will or should deposit 32 ounces of copper; and if iron be used, 28 ounces of iron should deposit 32 ounces of copper. Hence, in the plain language of a manufacturer, we should say that, with an odds-and-ends battery and raw zinc, there would be for every pound of copper deposited—

	s.	d.
16 oz. of zinc used,	0	4
16 oz. of copper dissolved,	1	0
	<hr/>	
	1	4

And when iron is used, the expense of depositing one pound of copper would be—

	s.	d.
16 oz. of iron, say	0	2
16 oz. of copper,	1	0
	<hr/>	
	1	2

Notwithstanding these results, Mr. Smee proves, by several fractional formulæ and an algebraic equation, that the cost of depositing a pound of copper is—

	s.	d.
By iron,	1	6
By odds-and-ends battery,	1	0*

To this it may be replied by the manufacturer, that in the first place, raw zinc or spelter used in the way described for an odds-and-ends battery would lose two or three times the quantity that is stated for every equivalent of copper; and secondly, that this form of battery is altogether unsuitable for manufacturing purposes, even when amalgamated scrap zincs are used; and as regards the calculation, it is not easy to see that, while a pound of copper dissolved from the positive electrode originally costs 1s., it could notwithstanding be deposited by the destruction of 1 lb. of zinc, not including acid, &c., at the expense of only 1s. It ought always to be remembered, that for manufacturing purposes the surface upon which the metal is to be deposited in general amounts to several square feet. The article may be, for example, a large ornamental vase, having 4 square feet of surface. An odds-and-ends battery, or an iron single pair battery, would be too weak. To deposit, with a separate battery, upon a surface such as that of the vase, it requires two or three pairs of plates to give what we may call economical power.

RECOVERY OF MERCURY FROM WASTE ZINC.—The general practice of manufacturers when the scraps of zinc become small and unsuit-

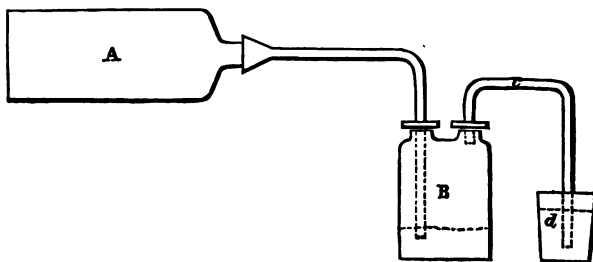


Fig. 34.

able for the battery, is either to treat them, as referred to at page 29, or to distil the mercury from the zinc. This is done by put-

* Smee's *Elements of Electro-Metallurgy*, 3rd Edition, p. 112.

ting the scraps into an iron retort, subjecting it to a red heat, and allowing the beak or tube of the retort to dip into water (Fig. 34). A, an iron bottle having a tube, fitted to neck with a screw, leading to B, a Woulffe's bottle, where most of the mercury collects; c is a tube leading to d, a small vessel filled with water to secure against any escape of mercury. The bottle A should not be more than half filled with zinc scrap. The mercury distils over, and condenses in the water. The zinc left in the retort is found to be so impure as not to be fit to melt and roll again, but it may be used in the composition of common brass. Dr. De la Rue, in a communication to the Chemical Society,* gives the results of several analytical experiments upon scrap zinc. Before distillation the scraps usually give the following results in 100 parts :—

Zinc,	67·3
Mercury,	4·3
Dross and loss,	28·4
								<hr/> 100·0

The composition of the zinc left after distillation is given as—

Zinc,	90·
Iron,	2·56
Lead,	6·
Copper,	1·44
								<hr/> 100·00

COMPOUND CELL PROCESS.—Another method of economising power was proposed by theorists in what is termed the *compound cell system*, by which it was said that the electricity passing through a series of cells would be able to produce the same quantity of work in every cell with no more cost. This plan may be illustrated thus :—

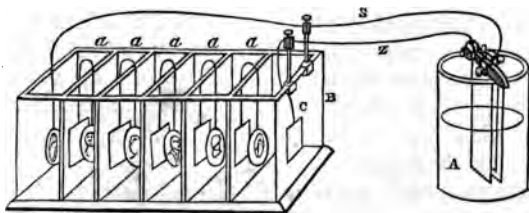


Fig. 35.

* *Memoirs and Proceedings of the Chemical Society*, vol. II., page 393.

A is a Smee's battery; the wire z is conducting the electricity to the compound trough, which is composed of a series of water-tight cells, aa, and is connected with a piece of copper, c, forming a positive electrode; in the same cell, and facing this electrode, is a medal, connected by a copper wire to a piece of copper placed in the second cell, opposite which is another medal connected in the same manner with another piece of copper, and so on through the series, which terminates with a medal attached to the wire of the battery. The electricity from the battery passes through all these cells, and reduces its equivalent in each cell. Thus the solution of 32 grains of zinc in the battery would deposit 32 grains of copper multiplied by six times, or as many times as there are cells.

This is correct in principle, and at first sight seems to be exceedingly economical; but it is not so, for every cell adds so much to the resistance of the current, that intensity batteries must be used; so that, supposing we have a compound cell of six divisions, in which are placed six separate medals, it would require a battery of six pairs of plates to give intensity sufficient to overcome the resistance, and the same number of medals could be made of the same weight by six separate zincs, and in less than half the time they could be made by this compound arrangement, and with a less destruction of zinc. For large operations, where the articles receiving the deposit and the electrode are necessarily a good way apart, the process is altogether impracticable in a commercial point of view. This is one of the remarkable instances where theoretical possibility and commercial economy are at variance. This is an arrangement which may be suited to a magneto-electric apparatus, where there is great intensity and small quantity; the intensity may be thus utilised and made to produce quantity by this compound cell (see page 53).

EFFECTS OF RESISTANCE.—At page 77 we mentioned, that if a single cell deposits 100 grains in a given time, and it be converted into a battery having the two electrodes in a solution of sulphate of copper, there will only be deposited in the same time 30 grains. This is caused by the extra resistance which the solution between the two electrodes in the decomposition cell, offers to the passage of the electricity, the amount of which corresponds to the amount deposited—the latter depending upon the former.

If we take two small plates of copper and amalgamated zinc, and place them in dilute sulphuric acid in contact, but not so close as to prevent the gas evolved from the copper plate to escape, say $\frac{1}{4}$ inch, and allow them to remain until there have been dissolved from the zinc 100

grains, and we call this practically the measure of the maximum amount of electricity which that surface of zinc and copper can give out in the time taken to dissolve the 100 grains; then, if the two metals in the acid be separated one inch and quarter, being connected by a wire or slip of copper above the liquid, and kept in action the same length of time as the former, there will be dissolved from the zinc only about 56 grains. If the wire in connection with the zinc and copper be extended and cut in the middle, and have a piece of copper attached to each of the ends the same size as the zinc plate in acid, and these be placed in another vessel containing a solution of sulphate of copper (as Fig. 5), and put an inch apart, and the whole kept in action the same length of time as before, it will be found in this case that only 10 grains of zinc are dissolved. From these experiments we see that the resistance of the one inch of acid between the zinc and copper in the battery, and the one inch of solution of sulphate of copper in the second or decomposition cell, is 90 per cent., the actual work being only one-tenth of the electricity which the zinc and copper are capable of giving.

INTENSITY.—If we now take another zinc and copper plate of the same size as the former, and arrange them in the acid solution, and connect them with the copper plates in the decomposition cell, as shewn in Fig. 36, and keep them in action the same length of time as in the former experiments, there will be dissolved from the zinc about 19 grains, and deposited upon the copper plate attached to the zinc in the decomposition cell 18 grains of copper.

If three zincs and coppers be arranged as described, and placed in the acid, there will be dissolved from the zinc plate 26 grains, and deposited upon the copper 25 grains. If six pairs zinc and copper be arranged as above, and placed in acid, there will be deposited 36 grains of copper, which we will also take as the measure of what is dissolved from the zinc; and if nine pairs of zinc and copper be used, there will be deposited

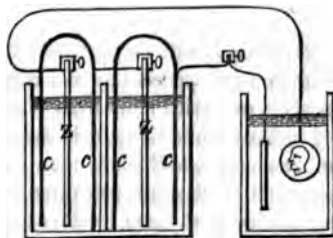


Fig. 36.

43 grains, and so on until the quantity dissolved from each zinc or deposited on the copper plate be 100, equal to that obtained by the close contact of the zinc and copper in acid, this will require upwards of thirty pairs of zinc and copper. It must be borne in mind that the

same quantity of zinc will be dissolved from every plate in the arrangement: thus, in nine pairs where 43 grains were deposited, there would be dissolved from every zinc in the battery 43 grains.

It will now be apparent that the use of several pairs in the battery is to overcome resistance, by which quantity is gained at the same time up to a given point; but quantity gained by this means is expensive. The 10 grains deposited by the single pair of zinc and copper only required 10 grains of zinc, but the 43 grains by the nine pairs would require $43 \times 9 = 387$ grains of zinc to be dissolved.

RELATIVE INTENSITY OF BATTERIES.—Different batteries have different degrees of power to overcome resistance—different intensities. The following experiments will illustrate this:—A single pair of a Wollaston's, Smee's, and Grove's batteries were fitted up as nearly equal in circumstances as the different arrangements would allow—each exposing the same surface of zinc, and connected with electrodes placed in a solution of sulphate of copper, first 1 inch, then 2 inches, 3 inches, and 4 inches apart—half an hour in each. They were then reversed, beginning with the electrodes at 4 inches, and coming to 1 inch. These experiments were repeated several times, and a mean of the whole taken: the results were—

	Wollaston.	Smee.	Grove.
Electrodes 1 inch deposited, . .	8.8 grains.	12.0	31.0
„ 2 inches „ . .	6.6 „	6.8	26.0
„ 3 inches „ . .	4.7 „	6.0	17.0
„ 4 inches „ . .	3.0 „	4.6	14.0

From this it will be seen that Wollaston's stands lowest in intensity, which is more apparent as the distance of the electrodes is increased. Smee's is one-third more than Wollaston's at 1 inch, and one-half more at 4 inches; while Grove's is three and a-half more than Wollaston's, and two and a-half more than Smee's at 1 inch, but four and a-half more than Wollaston's and three more than Smee's at 4 inches. If we take the mean of these results as a comparison of batteries, their value will stand as under:—

One of Grove's equal to three of Smee's, and to three and three-fourths of Wollaston's.

The following table gives the results of the different batteries,

arranged in series, kept in action the same length of time—namely, one hour; the battery plates were small, about 6 square inches exposed to acid, the electrodes twice the size of the battery plates:—

	One Pair.	Two Pairs.	Four Pairs.	Six Pairs.	Nine Pairs.
Grove's,	55	72	93	97	98
Daniell's,	15	35	60	77	86
Smee's,	11	19	29	41	58
Wollaston's,	8	15	24	33	48

This table gives results approaching to and in principle the same as the others: it will be observed that one pair of Grove's is equal to nine pairs of either Wollaston's or Smee's. It is also worthy of remark, that Grove's increases slowly in quantity above four pairs, the intensity being sufficient at four pairs to overcome the resistance offered to the current of electricity. For ordinary electrotyping intensity arrangements are unnecessary, except where the article upon which the deposit is being made is of such a character as will not allow the positive electrode to be brought close to it, or when there are deep cut objects, or any circumstance that increases distance and necessitates power to overcome the consequent resistance.

MODE OF SUSPENDING OBJECTS FOR COATING.—In beginning to operate in the art of electrotyping, the student often pauses, and asks the question, What is the best position in which a medal should be hung in the solution? Convenience has brought into general practice the suspending of it perpendicularly in the solution, having the positive electrode or pole facing it in a parallel direction; but to this method there are some objections. If, for instance, the porous diaphragm, or single-cell system be used for obtaining the medals, it is found that upon the lower portion of the medal the deposition is much thicker than upon the upper portion. Indeed, when even ordinary attention is not paid, the lower part becomes not only thicker, but studded over with round nodules of copper, or with lines composed of these nodules, while the upper part remains thin, and is covered over with what is termed the sandy deposited copper, in dark brown grains, capable of being rubbed off with the slightest friction. No doubt this is in a great measure

prevented by agitating the solution ; but it is inconvenient, and requires constant attention. To avoid this it was proposed to place the plates in

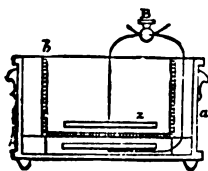


Fig. 37.

a horizontal position as Fig 37 ; but this method has never been much practised, probably, in the first place, from its great inconvenience, it not being easy to fix the two electrodes, as shewn in the figure, by suspension, as the zinc plate ought not to touch the bottom of the cell ; true it might be made to rest upon small pieces of stoneware or other non-conducting materials, which was generally done ; but this was found obstructive. In the second place, any sediment in the copper solution settled upon the medal, and caused a roughness which was not liked ; besides, porous cells, to suit this arrangement, were not easily obtained. Any cylindrical tube, such as a jelly-pot without a bottom, could be converted into a porous cell of this sort by tying a piece of bladder round one end ; but this did not avoid the other difficulties referred to, and such diaphragms soon gave way, and, so far as we are aware, this arrangement was never in use for manufacturing purposes.

When a separate battery is used, and the deposition of the medal is effected in a separate vessel, by having a copper positive electrode, the same inconvenience of irregularity in thickness of top and bottom parts takes place to a greater or less extent, according to the distance at which the two poles are placed. These inconveniences are known to all electrotypists, and the cause is rightly ascribed to the different densities of the solution. The reason why the solution becomes of different densities is easily understood in the single-cell process, there being no copper pole to maintain the strength of the solution ; as it becomes exhausted of copper by the deposition, the lighter portion floats on the top, and the heavier portion remains below ; and although crystals of sulphate of copper be suspended in the solution, as they dissolve the salt sinks by its gravity to the lower portion of the solution, and consequently we have a much more powerful deposit. But why the same should take place with a separate battery, where there is a positive electrode of copper being dissolved, just in proportion to the copper extracted from the solution by the medals, was for a long time not known.

NON-TRANSFER OF ELEMENTS.—And we claim for ourselves the credit of being among the first, if not actually the first, to find out the cause of this—at least, it was original on our part, at the same time the explanation is not yet acknowledged by theorists. We here give the outlines

of the first announcement of the discovery. Early in 1844 while employed in manufacturing electro-metallurgy, then in its infancy, the premises in which the operations were being conducted were daily visited both by the curious and the scientific of London. One day two gentlemen came in whom we soon perceived by their remarks were men of science. While looking into the plating solution which was filled with articles being covered with silver, one made the remark to the other, "How silently two distinct currents are passing in that solution, the silver in the one direction, the solvent in the other, yet nothing is visible to indicate that such is the case." "That, sir," we remarked, "is theory, but we find it is not so in practice—the solvent travels but not the metal;" at which remark he turned to his friend, saying loud enough for us to hear, "What notions workmen take." However, the other gentleman said, "If you have discovered what you say, it is worth laying before the Royal Society." This doubt and encouragement sent us back to a careful repetition of our experiments that had been going on for months, in order to lay the results before the Chemical Society. In the interim we mentioned the matter to the late Mr. Robert Murray, who told us that Professor Daniell and Miller had read a paper before the Royal Society upon a similar subject. Hearing this and before the contents of Professor Daniell and Miller's paper were known to us, we hurriedly drew up the results of our experiments and observations, which were read at a meeting of the Chemical Society on the 6th of May 1844, in hopes that if the discovery made by Professor Daniell and Miller was the same as ours, we should at least get credit for being original; but as the phenomenon discovered has never yet been acknowledged by other scientists there has been very little credit given to either party. We will reserve the further consideration of this non-transfer of the metallic element until we come to consider the theory of electrolysis based upon the facts of experience and observation, contenting ourselves in the meantime in saying, that so far as our observations have been made no metal is transferred, in any quantity, by the electric current, nor any element taking the position of the metal in an electrolyte, but that the acid element is always transferred equivalent to the electricity passing. It has been shewn that during the deposition of a metal, say copper, in electrotyping, the acid, when exhausted of the copper at the surface of the medal, is transferred to the positive pole, and dissolves from it its equivalent of copper; but this is not transferred by the electric current to the medal, but descends by its gravity to the bottom; hence it will be observed, that the solution next the medal will thus become exhausted of copper, and will consequently rise to the sur-

face from its greater lightness. There is no doubt a flow of stronger solution in a horizontal direction at the bottom, from the positive pole to the medal, and a flow on the top from the medal to the pole, caused by the lighter portion ascending; but this does not mend the evil: the light portion is increasing on the surface, and the heavier at the bottom, so that the whole solution soon becomes of different densities; and this constant current of the solution flowing up the surface upon which the deposition is taking place, causes the lines that are observed in deposits,

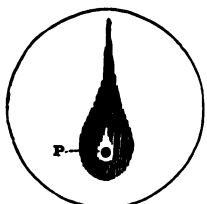


Fig. 38.

and which are sometimes very annoying. If a small hollow be in the mould, or even if a small portion of a plane surface resist the upward current of the solution, the metal will accumulate round the edge of the resisting portion, giving the deposit the appearance of having been made in a flowing stream, like a stone standing up in a current of water (Fig. 38). The black point in the centre represents the resisting spot, around which the deposit will thicken, causing a

ridge of metal to radiate to a point immediately above the resisting portion. These circumstances are much more annoying in solutions of gold and silver than in sulphate of copper, as will be noticed when we come to treat of plating and gilding. A point of grease or dirt, or small hole not cleaned out, hardly visible to the naked eye, will give a very prominent effect upon the plane polished surface of a piece of metal.

From these observations, the reader will now be able to answer the question—What is the best position to place a medal in the solution? To make it still more apparent—take a glass jar filled with a solution of sulphate of copper; place a piece of copper upon the bottom of the jar, and suspend the medal at the top, having their two faces parallel; connect them with a battery; in a short time the solution round the medal becomes exhausted, and even colourless, the medal covered with a dirty brown powder, and no further deposit will take place. But reverse the case: place the medal at the bottom, and the copper positive electrode at the top; the deposition goes on constant and smooth; the solution is maintained in the same condition as it was at the first, there being a constant transfer; the acid is transferred by the current from the medal at bottom to the copper pole at top: the sulphate of copper formed descends by its gravity to the medal. There are, no doubt, as already stated, objections to placing the medal under the positive electrode, such as the impurities in the copper getting disintegrated, and falling upon the surface; but a piece of cloth wrapped

round the pole prevents this. However, when a fine surface is wanted, care ought always to be taken to have clean solutions filtered and kept covered from dust; and when the single cell is used, the crystals of sulphate of copper should be suspended in a fine linen bag, or the shelf holding them be lined with linen. Although, as already stated, this is the best method in principle, very few practise it, because of the trouble attending the arrangement of the electrodes in this position. When the medals are small the annoyances from perpendicular suspension by unequal density are not great; but if the surface of the article which is being deposited be large—say eight inches or upwards—the difference in the thickness of the lower and upper portion of the medal, if care be not taken, is very great. When suspended perpendicularly, the position of the article should be shifted several times, making the upper portion the lower, besides occasionally stirring the solution, or shaking the article. Indeed, when convenient, the article receiving the deposit should be kept as much in motion as possible, as it regulates the deposit, making it smoother and less brittle.

CRYSTALS OF COPPER ON ELECTRODES.—It will be found, from the reasons stated above, that the sulphate of copper solution becomes so saturated round the positive electrode by the transferred acid, that the electrode often gets coated over with crystals of sulphate of copper, which adhere with great tenacity, and stops the electric action. Under such circumstances, it is only necessary to clean the electrode from the crystals and to add a little water to the solution, which will prevent a recurrence of the crystals for a time. But the stirring of the solution occasionally will do much to prevent this crystallisation.

BRONZING.

WE have already mentioned that when a medal has been made from a metallic mould, protected by a little wax dissolved in turpentine, it retains its bright copper lustre for a long time, even when exposed to the air; but generally the copper medals and other objects are very liable to tarnish, for which reason it is usual to give them a coating of bronze, that they may acquire a permanently agreeable appearance.

BROWN BRONZES.—Bronzing is effected by several very simple methods, the most common of which is the following:—

Take a wine-glass of water, and add to it four or five drops of nitric acid; with this solution wet the medal (which ought to be previously well cleaned from oil or grease), and then allow it to dry; when dry impart to it a gradual and equable heat, by which the surface will be darkened in proportion to the heat applied.

ANOTHER METHOD.—Make a thin paste of crocus and water: lay this paste on the face of the medal, which must then be put into an oven, or laid on an iron plate over a slow fire; when the paste is perfectly reduced to powder, brush it off and lay on another coating; at the same time quicken the fire, taking care that the additional heat is uniform; as soon as the second application of paste is thoroughly dried, brush it off. The medal being now effectually secured from grease, which often occasions failures in bronzing, coat it a third time, but add to the strength of the fire, and sustain the heat for a considerable time: a little experience will soon enable the amateur to decide when the medal may be withdrawn; the third coating being removed, the surface will present a beautiful brown bronze. If the bronze is deemed too light, the process can be repeated.

Another very simple method is this: After the medal is well cleaned from wax or grease, by washing it in a little caustic alkali, brush some blacklead over the face of it, and then heat it in the same way as described for crocus; or a thin paste of blacklead may be used, and the processes already referred to be repeated until the desired brown tint is

obtained. In this kind of bronze a little Hematitic iron ore, which has an unctuous feel, may be brushed over the face of the bronze, by which a beautiful lustre is imparted to it, and a considerable variety in the shade may be obtained. In the brown bronzes the copper is slightly oxidised on the surface.

BLACK AND OTHER BRONZES.—A very dark-coloured bronze may be obtained by using a little alkaline sulphide (sulphide of ammonia is best). The face of the medal is washed over with the solution, which should be dilute, and the medal is dried at a gentle heat. It should afterwards be polished by a hard hair brush. Hydrogen sulphide gas is sometimes employed to give this black bronze; but the effect of it is not so good, and the gas is very deleterious when breathed. In these bronzes the surface of the copper is converted into a sulphide. Dipping into a weak and hot solution of cyanide of potassium, and exposing to the air will give a dark bronze according to the time exposed; wash out and dry.

Many metallic solutions, such as weak acid solutions of platinum, gold, palladium, antimony, &c., will impart a dark colour to the surface of medals when they are dipped into them. The medal after being dipped into the metallic solution is to be well washed and brushed. In such bronzes the metals contained in the solution are precipitated upon the face of the copper medal, which effect is accompanied by a partial solution of the copper.

GREEN BRONZES.—Green bronzes require a little more time than those already described. They depend upon the formation of an acetate, carbonate, or other green salt of copper upon the surface of the medal. Steeping for some days in a strong solution of common salt will give a partial bronzing which is very beautiful, and if washed in water, and allowed to dry slowly, is very permanent. Salammoniac may be substituted for common salt. Even a strong solution of sugar alone or with a little acetic or oxalic acid, will produce a green bronze; so also will exposure to the fumes of dilute acetic acid, to weak fumes of hydrochloric acid, and to several other vapours. A dilute solution of ammonia allowed to dry upon the copper surface will leave a green tint, but not very permanent.

Electrotypes may also be bronzed green, having the appearance of ancient bronze, by a very simple process: Take a small portion of bleaching powder, place it in the bottom of a dry vessel and suspend the medal over it, and cover the vessel: in a short time the medal will take

on a green coating, the depth of which may be regulated by the quantity of bleaching powder used, or the time that the medal is suspended in its fumes; of course any sort of vessel, or any means by which the electrotype may be exposed to the fumes of the powder, will answer the purpose: a few grains of the powder is all that is required. According as the medal is clean or tarnished, dry or wet, when suspended, different tints with different degrees of adhesion will be obtained.

The green bronzes are generally applied to figures and busts.

These directions and hints will enable the student to vary his bronzes. Practice will give him perfection, and enable him to fix upon that which best pleases his taste. Scarcely two electrotypists agree upon the same method of bronzing, but differ in some little details of practice or on some point of taste. Each prefers the plan that has given to him his best results, and which he can hardly impart by description to another. A thin varnish washed over the surface keeps the colour from changing, but most people prefer to allow them to darken by exposure to the atmosphere.

Should the electrotypist wish to coat the copper medal with another metal, as silver and gold, directions will be given under plating and gilding how to proceed to effect his purpose.

MISCELLANEOUS APPLICATIONS OF THE PROCESS OF COATING WITH COPPER.

BESIDES the applications and processes which we have described under the general term of electrotyping, there are various applications of the process for depositing metals upon other substances, which have been, and may be still more usefully applied. We may, at a trifling cost, impart a coating of copper to cornices for decorating buildings, to terra cotta, to engravings on wood, &c. Cloth may also be easily covered, and made to assume the appearance of a sheet of copper, having the lightness and pliability of cloth. Lace has been covered with copper, and used for battery plates, and has also been gilt and made into beautiful ornaments. Table covers with metallic ornaments richly gilt, and book covers, have all been tried with more or less success, although they have not yet been profitably produced.

COPPERED CLOTH.—Cloth covered with copper was prepared a few years ago in considerable quantity, and an attempt was made to introduce it as a covering for roofs, railway waggons, &c., where there was any danger of fire from sparks from chimneys and locomotives. And so far as its being a protection against fire from such causes it was experimentally proved successful. Cloth covered with copper, to the thickness of tissue-paper, and well washed and dried out of a weak solution of sulphate of ammonia, and put upon a roof, and a quantity of small pieces of red-hot charcoal thrown over it, did not even char the cloth under the glowing charcoal. The copper seemingly conducted the heat so rapidly over its surface that no burning took place; but the price required for cloth so covered compared with that of the ordinary materials used for covering waggons, &c., prevented its adoption; also when the covering had to be often removed and cast about, as those used for waggons generally are, the copper hardened and cracked. There were also other difficulties, such as the kind of cloth. Linen and cotton did well, but they required a good coating of copper to make them water-tight, which increased the cost. The best material, so far as the

coating of it was concerned, was a cotton felted with india-rubber solution. We have covered pieces of such cloth twelve yards long by one yard wide with 6 lbs. of copper; however, after a few months exposure upon a roof, or lying past, the india-rubber upon the cloth decomposed, and rendered the covering too weak. Nevertheless, what have been difficulties to one party may be overcome by others; and we have still hope that when these practical and commercial difficulties are overcome, the application of electro-covered cloth will be of great use for many purposes, both at home and abroad. The operations of coating cloth with copper were the same as described for the wax medals: the cloth was brushed over with a polish of blacklead, and then stretched upon a frame of wood having a copper band round it, in which were placed small hooks or pins, and the cloth was attached to these. A vat, four feet deep and twelve yards long, was made of brick and cement; this was divided lengthwise by a wooden frame, with panes the same as a window, which were filled in with unglazed earthenware plates, cemented by marine glue, and the whole made water-tight. Into one division of the vat were placed the dilute acid and sheets of amalgamated zinc; in the other the solution of copper, in which was placed the cloth upon the frame. The arrangement was so perfect that we have often seen pieces of cloth, twelve yards long by one yard wide, completely covered with copper in one hour, not having more than 4 ounces on the square yard.

A similar thickness is quite sufficient for other surfaces, such as woodwork, cornices, &c., to stand mere exposure to the atmosphere, and may be produced at the same rate, about 2s. 6d. per pound of copper.

Besides these applications, many others have been suggested and tried with variable success. Some have probably been abandoned too soon, others have had both capital and talent applied, and success is yet to come. We shall only name a few of these applications.

CALICO PRINTERS' ROLLERS.—So early as 1841 various means were tried to apply the electro-deposition of copper to the preparation of rollers for printing calicoes, both by depositing the copper upon wax or other moulds, to make an entire roller of copper, or to deposit a surface of copper on other metals, such as iron or brass; but none of them have yet commercially succeeded. To make an entire roller is much more expensive, without an equivalent advantage over the ordinary method of casting, rolling, and boring. To deposit a layer of copper on iron is attended with many practical difficulties, both in protecting the iron from the acid solution for so long a time as is required to deposit the proper thickness, and in securing the adhesion of the two metals during the

subsequent operations. It requires a deposit of about five-sixteenths of an inch in thickness to allow for turning before engraving. There is then the annealing to soften the copper, &c., which interferes with the adhesion of the two metals, probably from their different rates of expansion and other causes. Similar objections may be made to the coating of brass rollers with copper.

That the idea is not yet abandoned by the electro-metallurgists upon the Continent is manifest by the following, which we copy from the *Chemical News*, November, 1874:—"Many attempts have been made in this direction by Lockett, L. Huguenin, and Schlumberger. One of the defects of the copper-covered rollers was that they were capable of losing their true form, an accident easily remedied upon a cylinder of copper, but not upon those of coppered iron. Schlumberger cleanses the iron cylinder with a concentrated alkaline lye, washes well in water, and goes over the whole surface with the file. The surface is then very bright, and is not to be touched with the fingers or soiled with the breath. It is then plunged in an alkaline bath composed of one part sulphate of copper, dissolved in twelve parts water, to which is added three parts cyanide of potassium, four parts carbonate of soda, two parts sulphate of soda, dissolved in sixteen parts water. Or ammonia three parts, acetate of copper two parts, dissolved in ten parts of water, to which is added three parts cyanide of potassium, four parts carbonate of soda, two parts sulphate of soda in ten parts water. The cylinder is allowed to remain twenty-four hours in one of these baths, subject to the action of a battery of four or six pairs, till the surface is coated with a slender but adherent layer of copper. It is washed and cleaned with pumice stone. If in this operation the iron should be laid bare in any part, the cylinder must be anew submitted to the alkaline bath. As soon as the coating of copper is uniform it is washed in acidulated water and immersed in an acid bath of sulphate of copper. This bath is composed of a solution of sulphate of copper at 20° B. (30° Twad.), to which 1-300th of its volume of sulphuric acid is added to facilitate the solution of some metallic copper, which is also immersed in the bath for the purpose of maintaining the solution in a uniform state of concentration. Here the cylinder is left till the layer of copper has attained the desired thickness, a galvanic current being kept up by a battery of four pairs. If the temperature is between 15° and 18° C. (59° and 64° Fah.), three or four weeks are required to produce a deposit of three quarters of a millimetre (fully one-fourth inch) in thickness. The cylinder is turned one-fourth round daily, to change the portion of it which faces the sheet of copper used as a positive electrode."

We quote this from the work named to illustrate what may be often observed, that practical matters tried here and abandoned are often brought up by philosophers in other countries as new things. The description of the process here given is certain to produce one of the defects we have stated—want of adhesion of the two coatings of copper. To lift the roller from the cyanide solution of copper, and put it into acidulated water by way of washing, will cause a film of cyanide of copper to be formed over the surface, which prevents perfect adhesion of the next deposit. It is better to wash the roller out of the cyanide solution by swilling it in a warm solution of carbonate of soda, and then in water, and put from this into the solution of sulphate of copper. This should be done quickly to avoid any tarnish, and if two or three batteries of one pair, each zinc plate being 12 by 14 inches square, be attached to different parts of the roller, one-fourth of an inch thick of copper may be deposited in one week. The putting into the solution pieces of copper to keep up its concentration where there are copper electrodes is certainly new. With free sulphuric acid in a sulphate of copper solution, if the electrodes are larger than the roller, the solution will become more concentrated without pieces of copper being put into it; and if these are not connected with the electrodes their influence is *nil*. However, apart from the manner of depositing, let us consider the practical and commercial advantages or disadvantages of such rollers. One disadvantage experienced is, the copper deposited by even a four-pair battery is much softer than the ordinary copper roller, so that the pattern is sooner worn out, and has to be oftener deepened.



A printing roller is a hollow cylinder of copper, in section like Fig. 39, having a diameter of say $5\frac{1}{2}$ inches, the thickness of the copper being about an inch, and the roller about 36 or 40 inches long. Now, suppose we take a cast-iron roller of similar dimensions, say 36 inches in length, and deposit upon it, by the process described in the extract, the $\frac{5}{8}$ of an inch of copper, allowing $\frac{1}{8}$ to be taken off by a lath, to prepare and smooth it for the engraving. The cost of this will be, taking the whole at the lowest estimation—

	£	s.	d.
Iron roller, weighing say 1 cwt., prepared for deposit, .	0	10	6
$\frac{5}{8}$ of an inch copper, weighing 38 lbs., at 1s., .	1	18	0
Zinc dissolved in a four-pair battery, 40 lbs. from each } plate, $4 \times 40 = 160$ lbs. amalgamated, say 7d. per lb., }	4	13	4
300 lbs. of acid for battery, at $\frac{1}{2}$ d., .	0	12	6
Labour, cleaning, attendance, &c., say .	0	10	0
	8	4	4

The copper when ready for engraving will weigh 30 lbs., and will cost 5s. 1½d. per lb. When a pattern is done with it is removed by the turning lath and another pattern put on; each pattern removed takes away from 4½ lbs. to 5 lbs. of copper; then the utmost number of such removals and renewals of pattern cannot exceed five, not including first pattern, so that each pattern will cost £1, 7s. 4½d. Of course, after the copper is too thin to have a pattern renewed, more copper can be deposited upon this, and the iron base do for many times over; still, ¼ inch of copper deposited by the process referred to will cost £7, 14s. 4d., or £1, 5s. 8½d. per pattern.

The ordinary copper roller of the same dimensions—36 by 5 inches, and 1 inch thick—weighs on an average 125 lbs., costing 1s. 1d. per lb. = £6, 15s. 5d. This copper roller will stand fourteen removals and renewals of pattern—that is, fifteen patterns will be printed off this one roller; when too thin for further removals, about ⅔ of an inch thick still remains and will weigh 60 lbs., worth 10½d. per lb. = £2, 12s. 6d., which, being deducted from the original cost, leaves £4, 2s. 11d. as the cost of fifteen patterns—5s. 6½d. each pattern—against £1, 7s. 4½d. by the electro process, or if roller is renewed, £1, 5s. 8½d.

ETCHING OF ROLLERS.—Another application of the process to printers' rollers was to plate the surface of the roller with a thin coating of silver for the purpose of etching. The engraving is then made through the silver coating; the roller is next passed through weak nitric acid, which acts upon the exposed copper, the silver taking the place of varnish in ordinary etching; but practical difficulties have caused the abandonment of this application. One of these is, that there is a galvanic action between the silver and copper that causes the copper to be acted upon by the acid under the edges of the silver coating.

GLYPHOGRAPHY.—A process which Mr. Palmer, the inventor, named Glyphography, has been very successful. The principle of the invention consists in depositing copper in the grooves or engravings made in a layer of some soft substance spread on a sheet of copper, and covering the whole with a sheet of electrotype copper. The counterpart of the engraving thus produced is used for printing from in the same manner as letterpress printers' types or woodcuts. It may therefore be called a mode of stereotyping, with this difference, that it is made directly from the drawing by the artist. The drawing, however, must be made in a particular way, which, with the other necessary manipulations, is thus given by Mr. Palmer:—

"A piece of ordinary copper plate, such as is used for engraving, is stained *black* on one side, over which is spread a very thin layer of *white* opaque composition, resembling white wax both in its nature and appearance; this done, the plate is ready for use.

"In order to draw properly on these plates, various sorts of points are used (according to the directions here given), which remove, wherever they are passed, a portion of the white composition, whereby the blackened surface of the plate is exposed, forming a striking contrast with the surrounding white ground, so that the artist sees his effect at once.

"The drawing, being thus completed, is put into the hands of one who inspects it very carefully and minutely, to see that no part of the work has been damaged or filled in with dirt or dust; from thence it passes into a third person's hands, by whom it is brought in contact with a substance having a chemical attraction or affinity for the remaining portions of the composition thereon, whereby they are heightened *ad libitum*. Thus, by a careful manipulation, the *lights* of the drawing become thickened all over the plate equally, and the main difficulty is at once overcome: a little more, however, remains to be done. The depth of these non-printing parts of the block must be in some degree proportionate to their width; consequently, the larger breadths of *lights* require to be thickened on the plate to a much greater extent, in order to produce this depth. This part of the process is purely mechanical, and easily accomplished.

"It is indispensably necessary that the printing surfaces of a block prepared for the press should project in such relief from the block itself as shall prevent the probability of the inking-roller touching the interstices of the same whilst passing over them; this is accomplished in wood engraving by cutting out these intervening parts, which form the lights of the print, to a sufficient depth; but in glyphography the depth of these parts is formed by the remaining portions of the white composition on the plate, analogous to the thickness or height of which must be the depth on the block, seeing that the latter is, in fact (to simplify the matter), a *cast or reverse* of the former. But if this composition were spread on the plate as thickly as required for this purpose, it would be impossible for the artist to put either close, fine, or free work thereon; consequently the thinnest possible coating is put on the plate previously to the drawing being made, and the required thickness obtained ultimately as described.

"The plate thus prepared is again carefully inspected through a powerful lens, and closely scrutinised, to see that it is ready for the *next stage* of the process, which is to place it in a trough and submit it

to the action of a galvanic battery, by means of which copper is deposited into the indentations thereof, and, continuing to fill them up, it gradually spreads itself all over the surface of the composition until a sufficiently thick plate of copper is obtained, which on being separated will be found to be a perfect cast of the drawing which formed the *clichée*.

"Lastly, the metallic plate thus produced is soldered to another piece of metal to strengthen it, and then mounted on a piece of wood to bring it to the height of the printer's type. This completes the process, and the glyphographic block is now ready for the press.

"It should, however, have been stated previously, that if any parts of the block require to be *lowered*, it is done with the greatest facility in the process of mounting."

This process has, however, not come into much use as a substitute for wood engraving, in consequence of the impossibility of finding a suitable varnish for the use of the artist or engraver. It has, in fact, given way to another process, also embraced in Mr. Palmer's patent, which is worked thus:—A copper plate is etched by the process commonly employed by engravers, the lines being cut into the copper with a bold stroke. The lines are then bitten deeper by nitric acid. The etching is made *direct*, not *reversed*, as it is upon a plate that is to be worked at the copperplate press. When the engraving is ready, the etching varnish through which the drawing is cut is covered with a conducting substance, and an electrotype plate is deposited upon the etching. When this is removed from the mould, it requires to be trimmed, for it is impossible to etch a plate, or to bite the etching, so that all the lines shall be exactly of the same depth. To remedy this, the face of the electrotype is levelled by grinding and burnishing. The following instructions for artists are published by the patentee:—

INSTRUCTIONS ON GLYPHOGRAPHY FOR THE AMATEUR.—"The amateur must remember that he is producing a work of art for the surface press, and not for copperplate printing.

"The drawing or etching should not be made with lines of equal thickness in all the tints. If it is so treated with a *thick* line, and if the cross hatching be kept of the same strength as the principal line, it will appear like a coarse pen-and-ink drawing. If it is treated in the above manner with a *fine* line, and the work laid very close, it will have the appearance of one of the old etchings. The amateur, therefore, will do well to remark, that it is only by a judicious mixture of bold and delicate work that beauty of style can be obtained;

and as the darkest shades are generally foremost, and become gradually lighter to the distance, so that the darkest or nearest tones should generally be formed by the boldest work, and gradually increase in delicacy to the offscape.

"Etching is a process nearly resembling drawing with a very fine pen or pencil, and should be proceeded with as follows:—

"Having obtained a polished copper-plate with an etching ground properly laid, proceed to put your design upon the plate.

"If it is a print or miniature that is being copied, you must make a sketch or tracing of the same with a blacklead pencil: it must then be traced on to the plate, remembering always that the proof from the block will be in the same position as the etching; and that nothing must be etched or written backwards, as for the ordinary copperplate printing.

"In order to trace the object on to the plate, take a piece of transfer paper,* place it face downwards upon the plate, secure the corners with a piece of wall wax or paste, or hold it steadily down, if there is not much to trace; then place on your sketch or tracing, go over the outline with your etching-needle or a very hard blacklead pencil, removing a corner at a time to see that all is correctly transferred and nothing omitted, or that the outline be not too heavy and thick, in which case you must trace lighter.

"Having thus got your subject, as it were, sketched upon the plate, proceed in all respects with your etching needle as if making a drawing with a blacklead pencil, only working more firmly, taking care always slightly to cut the copper.

"Be careful not to try to form the dark touches and the *black* parts of the subject with a number of lines crossing and recrossing each other, but scrape them away entirely with the point of your penknife, or any other convenient instrument.

"In commencing the etching of a view, it is usual to begin with the offscape, etching the same as neatly and as close as *the nature of the printing will admit*, working more firmly and boldly in every progressive tone, until you reach the foreground. In portraits it is usual to commence with the eye; and in draperies at the top, working downwards.

"Owing to the great difference between surface and copperplate printing, depth of tone should be sought as much from the breadth

* To prepare the transfer paper, take some thin post or tissue paper, rub the surface well with blacklead, vermilion, red chalk, or any colouring matter: wipe this preparation well off with a piece of clean rag, and it will be ready for use.

or thickness of the lines as from laying them close together; and, on the contrary, lightness of tint must be obtained by the distance of the lines from each other, as well as from their delicacy.

"If you make a false line, or wish to efface any portion of the work, a little Brunswick black (which can be procured at most oil and colour shops), spread thinly, may be used to stop it out; or rub a little of the superfluous ground from the side of the plate with a camel-hair pencil and turpentine: when this is dry the work can be re-etched and finished at pleasure."

This last process has afforded some excellent work in the shape of maps, among which we may cite the *Penny Atlas*, published by Messrs. Chapman and Hall. Among subjects of a more picturesque nature executed by glyphography, we may instance Mr. George Cruikshank's etchings of *The Bottle*. These are sufficient to shew that the art of electrotyping engravings promises to be hereafter of importance in the fine arts.

COPYING OF COPPER AND STEEL PLATE ENGRAVINGS.—The electro-metallurgical process for taking copies of engravings was first successfully applied to manufacturing purposes by Dr. Warren de la Rue in his extensive manufacture of cards, &c.; but the process was soon afterwards taken up by others and extended. Engravings of all sizes and every degree of excellence have been copied by the electrotype process. The process may be performed exactly in the same manner as described for copying a penny-piece, page 56, by making an electrotype mould on which, of course, the engraving appears in relief—from this mould any number of electrotype copies may be taken; or they may be copied as described under moulding by gutta percha, by placing the engraved plate in a press and laying upon it a sheet of gutta percha, heated to 212°, putting upon this a flat piece of metal, and then subject the whole to a heavy pressure for a few hours, then blackleading the gutta percha mould and taking from it a copy by the battery. The defect of such copies, however, was the softness of the copper—the engraving soon became blunt or worn. However, this defect has been overcome by depositing upon the surface of the electrotyped engraving a film of iron, as described in page 107, which imparts to it all the advantages of a steel plate; indeed, an ordinary copper engraved plate need not be copied, but coated with iron in the manner to be described.

Steel-plate engravings are still preferred for very fine work; and for a long time there was great difficulty in taking a good electrotype

from a steel plate. A mere pressure mould is liable to defects: and putting the steel plate in a sulphate of copper solution to copy by the battery, is soon destroyed by the acid; to prevent this, alkaline solutions of copper were used to cover the steel plate, to protect it from the action of the acid when put into the sulphate solution as referred to, page 98, but the two coppers did not always adhere. However, the following process may be adopted with success:—Solder a strip of copper on the back of the steel plate, then coat over the back and copper strip with copal varnish, and allow it to dry; wash the face of the engraving with a weak alkaline solution, and then connect it by the copper slip to the zinc of a battery, and put it into a solution of cyanide of silver (see Plating), when there is deposited a coating of silver; allow this to proceed until it is about the thickness of a visiting card. This silver is easily removed from the steel plate, and forms a perfect mould of the engraving, and the engraving is cleaned and laid aside. This silver mould is prepared in the same way as for taking fine electrotypes (page 76); and copper deposited upon it to a proper thickness, when separated from the silver mould, will form a *fac simile* of the steel engraving; two or more copies may be made if necessary. A film of iron is now deposited upon the surface of the copper plate, which imparts to it the useful properties of the steel plate, and which, as already stated, may be renewed from time to time as required.

There is another sort of printing or embossing by electrotypes, which has been practised for some years, and which is made more valuable by coating the type with iron; this is for embossing cards, boards of books, &c. Thirty years ago we made a thick electrotype of a skin of morocco leather, depositing directly upon the skin, which was used as a print for embossing other skins, giving them the appearance of morocco; this kind of embossing has been extensively used, and books bound with such skins have all the appearance of morocco leather.

STEREOTYPING.—As already stated, once the idea of applying the electrotype process to copying engravings, &c., was made known, it was soon extended and defects remedied; and this has taken place to such an extent that almost every printer of engravings and publisher of any extent has adopted the process, so that a great many of our most popular illustrated publications are the product of the electro-metallurgical art—both the letterpress and illustrations. The process may be thus performed, although different parties have different

modifications in proceeding, and little practical differences suggest themselves to every operator: The *forme* or page of a book set up in type, which may include a wood engraving, is fixed upon the upper plate of a screw-press face downwards; a plate of metal the size of the *forme*, having a rim round it to the depth of about $\frac{3}{8}$ of an inch, is filled to the edge of the rim with prepared wax, and laid flat in the press directly under the suspended *forme*, which is brought down by the screw upon the wax, the rim of the mould being so arranged as to prevent the forme of types being pierced deeper than is required; after standing until the wax hardens, the *forme* is raised, and there is thus formed a complete mould of the page, which is carefully removed from the plate, and a broad slip of copper slightly warmed is laid upon the back of the mould, which becomes embedded in the wax and adheres when cold. The face of the mould is now brushed over with fine blacklead, until the whole has a metallic lustre. It is then attached to the zinc terminal of a battery, and immersed in a sulphate of copper solution; the battery may be a single cell or separate pairs, as the party thinks best, only the plates should be large, and so arranged that the copper deposited is of good quality and takes little time. About forty-eight hours should give a sufficient thickness for being removed from the mould; it is then cleaned and backed up with an alloy to give it sufficient strength for the fatigue of working. The face of the copper is cleaned with an alkaline solution, and made bright, and there is then deposited upon this a bluish of iron, by the following process: Make a solution of proto-sulphate of iron (copperas) or protochloride of iron, in which is dissolved some salammoniac (see Deposition of Iron). An iron plate is used as an electrode; the type is attached to the zinc terminal of a battery of four pairs, and suspended in the iron solution for only a few seconds; a deposition of iron takes place over the surface or face of the type as hard as cast steel, and the type thus prepared will retain its sharpness for a long time; and whenever the iron begins to wear off, the type is cleaned and passed through weak hydrochloric acid, which removes the iron, and prepares the type for a new coating of iron, then it is as good as at first; and this can be repeated as often as required, the print retaining its original sharpness.

COATING OF GLASS AND PORCELAIN.—This is done by putting a fine coating of copal varnish over the glass, then blackleading it, and depositing the copper. Another method has been proposed, namely, to make a varnish of two parts asphaltum and one part mastic, by

fusing these together, and when cool dissolving the mixture in spirits of turpentine to a syrupy consistence. To prevent the deposit coming off the glass, the vessel is first corroded by the fumes of hydrofluoric acid. A solution of gutta percha in benzole has also been proposed as a varnish for fixing on the blacklead and deposit.*

Retorts, basins, and other chemical vessels are sometimes covered with copper for their protection during boiling and evaporation. China saucepans have also been made and covered with copper to take the place of tinned copper vessels; but the adhesion of the metal upon these substances, even when we attempt to secure it by the means above referred to, is never perfect, and after a short use the deposit of copper loosens from the vessels. There is then great liability for liquids to get between the coating and the vessel, and when heat is afterwards applied these liquids, saturated with verdigris, boil out. Consequently such coverings are not well adapted either for culinary purposes or delicate chemical operations. They have, notwithstanding, been highly recommended; and the practice of covering the bulbs of large plain retorts, &c., may be useful in a few large manufacturing operations, but our experience is certainly not favourable to their general use.

Mr. John Ridgway, of Cauldon Place, Staffordshire, china manufacturer, patented certain improvements in the method or process of ornamenting or decorating articles of glass, china, earthenware, or other ceramic manufactures. In the specification of his patent, Mr. Ridgway states that his first object is to apply a new glaze, which shall enable the metallic coating to adhere firmly by capillary attraction, and give affinity for copper as a first coating. In pursuance of this, he first submits the article to an alcoholic solution, or a gelatinous solution. He then brushes over it an impalpable powder, composed of half carbide of iron and half sulphate of copper. The article thus treated is then to be corroded by the fumes of hydrofluoric acid and smoothed, by brushing it over with silver sand, or by the scratch-brush; but when the shape and nature of the article will not admit of this, it is to be plunged into a liquor, consisting of 6 quarts sulphuric acid, 4 quarts aquafortis, $\frac{3}{4}$ ounce muriatic acid, and 6 quarts water. Grease is to be carefully removed and a thin film of mercury is to be applied. The solution of copper consists of one sulphate of copper and four filtered water. Suitable solutions for silvering or gilding, are to be applied in accordance with the practice of electrotyping. The claim is not

* *Progress of General Science*, vol. II.; and *Pharm. Journal*, vol. VIII.

for the solutions or the coating, but to the application of "electro-typing," or electro-metallurgy, to the objects stated in the title, provided the articles be so prepared as to allow them to combine and form an alloy with them.

ON GALVANIC SOLDERING.—Among the many applications of the deposition of metals, there is one we have been often asked about, namely, if it would not be possible to solder different metals together by that process. The following article, which is taken from the *Technologist*, will give a full reply to all who may be still inquiring for this application :—

"Under the name of galvanic soldering, a process is known by means of which two pieces of metal may be united by means of another metal, which is precipitated thereon through the agency of a galvanic current. This mode of soldering by the 'wet method' has been often recommended in various periodicals relating to the industrial arts; but it has been objected that, practically speaking, the union between two pieces of metal could not be effected by means of a metal precipitated by galvanic agency. In order, however, to arrive at a definite conclusion upon this question, M. Elsner undertook the following experiments, the results of which are in favour of the practical use of the operation of soldering by galvanic agency. In conducting these experiments, the kind of battery known as Daniell's 'constant battery' was employed; and upon the end of the copper wire which formed the negative electrode a strong ring of sheet-copper was placed. This ring was cut asunder at one point, and the distance left between the several parts was about the sixtieth of an inch. At the end of a few days (during which time the exciting liquors were several times renewed) the space in the severed portion of the ring was completely filled up with copper regulus, which had been precipitated; and on partially cutting with a file through the part thus filled up, and examining it with a lens, it was observed to be very equally filled with solid and coherent copper.

"Another copper ring was then cut into two parts, and the two semi-angular segments thus obtained were placed with the faces of the sections opposite each other, and submitted to the action of a galvanic current. At the end of a few days the segments were united by the copper precipitated, thus forming again a complete ring. It was also found in this case, on removing with a file a portion of the thickness of the ring at the points of contact, that the spaces had been completely filled up by copper galvanically precipi-

tated, which had united the whole. On observing these points carefully with a lens, the regular deposition of the copper could be readily traced between the formerly separated portions of the ring.

"A third experiment was made in the following manner:—Two strong rings of sheet copper were laid with their freshly-cut faces one upon another, so that the two rings constituted a cylinder. These rings were surrounded by a band of sheet tin, which was coated with a solution of wax, so that the two rings were equally surrounded by a conducting material. Thus disposed, these rings were attached to the negative wire of the battery, and immersed in the bath of sulphate of copper. At the end of a few days the interior surface of the rings was covered with precipitated copper, and between the contact surfaces of the two rings copper was also precipitated. These rings had only been submitted to the galvanic current to such an extent as to cover their interior surface with a thin coating of precipitated copper, and yet they were already completely re-united, and formed a cylinder consisting of a single piece. The exterior conducting covering consisting of a sheet of tin, was of course removed before testing the cohesion or persistence of the galvanic precipitate. It may be remarked, that these rings, after being for a certain time in contact (during the galvanic action), together with the plate of copper upon which they rested, became so encrusted with precipitated metallic copper that some force was found necessary to effect their detachment from the copper wire.

"There would appear to be no doubt, then, according to the results obtained in the preceding experiments, that two pieces of metal may be firmly united by means of galvanically-precipitated copper—in a word, that soldering by galvanic agency is perfectly practicable. It will therefore be possible to firmly unite the different parts of a large piece of metal, and to make a perfect figure of them by galvanic precipitation of a metal (copper in ordinary cases). If solutions of salts of gold or silver were employed in as concentrated a form as those of copper above mentioned, there is reason to believe that galvanic soldering would also result. In fact, M. de Hackewitz states, that in some experiments on a larger scale which he undertook to obtain hollow figures by galvanoplastic means, he had remarked that galvanic union often took place between the pieces operated upon. M. Elsner states, that while conducting too powerful a current, the negative electrodes of copper, and even the plate of copper and ring of the same metal resting thereon, became covered with a deep brown substance, in the same manner as this occurs under similar circumstances in galvanic gilding, as is well known. After

several unsuccessful attempts to prevent the formation of this brown coating, M. Elsner found that it was possible to remove it entirely on immersing the articles covered therewith, during a few seconds, in a mixture of sulphuric and nitric acids. By this means the precipitated copper was made to assume its natural red colour. The possibility of practically effecting the operation of soldering by galvanic agency may be explained in a few words, in a theoretical point of view. The article is, in fact, in an electro-negative state of excitation, whilst the zinc operates positively; the result is, that the faces which are placed opposite each other, when the ring has been cut, are negative—that is to say, in an electric condition of the same denomination. During the progress of the electrolytic decomposition of the metallic salt in solution (sulphate of copper in the above case), the electro-positive molecules of copper which are detached simultaneously arrange themselves upon the two opposite faces, and in the direction of the break. Now, from the moment that these molecules are deposited they constitute, with the piece, a homogeneous mass; and from that time act negatively upon the copper which is contained in the solution, and again precipitate copper in the form of regulus. This method of operation continues until the space which existed between the two separate pieces of metal is filled up with metallic copper; in fact, the layers of copper which become deposited in an equal manner upon the contiguous faces of the metal gradually diminish the distance which separated the latter, until at length the metallic layers which cross in the opposite direction meet each other; the result being that the whole of the break which originally existed between the faces will have disappeared, and become filled up with copper.

“With respect to the solidity (the degree of cohesion) of the galvanic soldering, it is the same as that of copper or other metal precipitated by galvanic agency. It will, moreover, be well understood that too energetic galvanic excitation must have an injurious influence upon the cohesion of the metal precipitated; and in this case precisely the same phenomena will be observed as those which have long manifested themselves in ordinary galvano-plastic operations.”—L. ELSNER: *Technologist*.

We mention another application of the electro deposition which might be extended.

GALVANO-PLASTIC NIELLO.—Niello, a peculiar style of enamelling, consists in engraving or stamping figures on a plate of silver or gold, and then filling the incised lines, or impressed pattern, with a sort of enamel, differing, however, from true enamel, which is a kind of glass,

This enamel is formed of a mixture of the sulphides of lead, silver, and copper. This mixture is of a black colour—hence the name *niello*, from *nigellum*, derived from *niger*, black—and when melted into the intaglio parts of a plate, gives it somewhat the appearance of an inked engraved copper-plate. A new kind of niello work has lately been introduced on the Continent, in which, however, the figures are not produced by an enamel of sulphide of silver, as in the true niello, but by a different coloured metal; thus on a plate of gold may be produced fine engravings, the lines of which are in silver, and so on. This can be effected in two ways: first, by covering the plate to be ornamented with a varnish exactly as is used in etching; the pattern or ornament is then to be engraved on this varnish, and the metallic surface etched out to the proper depth. The engraved plate is placed in a solution of the metal intended to form the pattern, and a deposit allowed to form in the usual way adopted in all galvano-plastic works. When the intaglio lines have been completely filled up by the deposited metal, the plate is removed from the solution and ground, when the pattern will be fully developed. The second method consists in sketching the ornament on a sheet of paper with lithographic ink, placing this with the side upon which the drawing was made upon a plate of silver or other metal to be ornamented, and pressing them together; the paper is now removed with water slightly acidified, leaving the ink adhering to the plate, which is to be sprinkled with sand. When the ink has fully dried, the sand is blown away; the plate is placed in a solution of the metal which it is intended should form the ground, and put in connection with the battery. By this means a deposit will be formed over the whole surface, except the parts protected by the ink; on the removal of the latter with alcohol or spirits of turpentine, &c., the original metal will be exposed, forming a pattern. Many highly ornamental and useful applications might be made of these processes. Instead of simply engraving the name and legend upon pieces of plate presented to persons, it might be put in in letters of gold at very little more expense.

We have, in our experiments in electrotyping, tried that of ornamenting by making copies of prints upon metallic surfaces, as follows:—Take an ordinary print, say of a woodcut, and paste it upon the metal on which the ornament is wanted, the picture or ink surface being next the metal, taking care that no air is left between the metal and paper. When the paste is perfectly dry, connect the article with a battery of three or four pairs, and put it into the coppering solution. Deposition takes place through the paper and paste, except where the ink

is; two or three minutes are enough to soften the paste; when the operation is completed, the paper being washed off, there is an exact copy of the picture. The amateur may try this on a plate of lead, by connecting the plate on which the picture is pasted with a battery, and putting it into a sulphate of copper solution, as he would do for an electrotrope, when he will get a copy of the picture on the lead: silver or gold pictures may also be made in this way. This process has never been applied to any useful purpose, but probably its publication may attract some one who may see it from a different standpoint, and put it to useful purposes, as we think there is something to grow out of it.

DEPOSITION OF METALS UPON ONE ANOTHER.

COATING OF IRON WITH COPPER.

BESIDES making articles of solid copper, we may at a small cost give a coating of copper to another metal, such as iron, which, if kept in a dry place, will retain the appearance of copper for any length of time. But in covering iron with copper, or any one metal with another, great care must be taken that a proper kind of solution be used.

It is a familiar fact, that if a piece of iron, such as the blade of a knife, be dipped into a solution of sulphate of copper, it receives a coating of that metal. This is often described as the result of galvanic action; but there is no more galvanic action in this than in any ordinary chemical combination—it is simply a case of chemical substitution; the acid that is in union with the copper having a stronger attraction for iron, leaves the copper and combines with the iron: the copper is left on the surface of the iron, but the two metals not having sufficient polar attraction to cause them to adhere so firmly as to exclude the action of the acid, the copper is undermined, and falls to the bottom of the solution as a powder. After some copper has fallen upon the surface of the iron, local galvanic action is induced between it and the iron; but this secondary action is altogether distinct from that which first takes place: at the end, the copper is all deposited, and the remaining solution is sulphate of iron.

Any solution that has the power to give a metallic coating to a metal when dipped into it, should not be used to coat that metal by electricity.

The degree of attraction of the common mineral acids for the ordinary metals is in the following order:—Zinc, iron, copper, nickel, silver, gold, platinum.

If the metal to be deposited be copper held in solution by an acid, say sulphuric acid, then iron or zinc cannot be coated with copper from this solution; the acid having a greater attraction for these metals, will leave the copper and combine with them as described above; but if the metal to be coated be any of those following copper in the above list, then no chemical action will take place, and no deposit will be made, except as the effect of the electric current introduced by the battery. This we believe is the cause why De la Rue, Spencer, and others, failed, at an early stage of the art, in their experiments in plating and gilding, as

they employed acid solutions, which are quite impracticable when used for depositing upon inferior metals. Under these circumstances, such solvents must be used which have a different relative attraction for the metals than the acids have. The substance first applied for this purpose is, after upwards of thirty years' experience, still found to be the best—namely, cyanide of potassium.

CYANIDE OF POTASSIUM.—This substance may be prepared by exposing ferrocyanide of potassium (yellow prussiate of potash) to a red heat in an iron crucible; then pounding the mass, and boiling it in alcohol of about spec. grav. 0.900: cyanide of potassium crystallises on cooling the resulting solution. But such a process as this, where hundred-weights of the salt are required, would be too expensive; and other and less expensive methods are adopted. With the ordinary method now in use there is a very common historical misapplication. As early as February, 1834, two brothers, F. and E. Rodgers, published in the *Philosophical Magazine* an easy process for making cyanide of potassium. After detailing the various processes then known, and others which they had discovered, they proceeded as follows:—"Cyanide of potassium may be prepared by exposing a mixture of anhydrous carbonate of potash and anhydrous ferrocyanuret of potassium to a moderate red heat in a covered porcelain crucible for about twenty minutes. The proportions employed should be nearly one equivalent of anhydrous carbonate of potash to one equivalent of the anhydrous ferrocyanuret of potassium: the process is very productive, for the weight of cyanuret of potassium obtained by this process is much greater than the weight of the cyanuret obtained by heating ferrocyanuret of potassium alone, owing to the cyanogen of the cyanuret of iron meeting with the potassium contained in the carbonate of potash, and, moreover, the process occupies less time; some carburet of iron always remains in the crucible."

As the cyanide of potassium was not then used for manufacturing purposes, the process for its manufacture was only known to the scientific chemist. When electro-metallurgy created a demand for cyanide of potassium, the late Professor Liebig recommended a similar process to that given above; his name therefore became, and still continues to be, associated with the discovery. He recommended eight parts by weight of dry ferrocyanide of potassium, and three parts by weight of carbonate of potash, which are the same proportions as given by the brothers Rodgers, but stated in a more popular manner.

Should the electro-metallurgist wish to make cyanide of potassium himself, the following method may be pursued:—

Ferrocyanide of potassium, pounded fine, is dried over a slow fire (we have found an iron plate, or clean shovel, to serve the purpose very well): it must be constantly stirred to prevent its forming a cake upon the hot iron; when perfectly free from moisture, eight parts is thoroughly well mixed with three parts of carbonate of potash, also well dried. Put a cast-iron crucible into the fire, and when it is red-hot nearly fill it with the mixture, and keep up the heat by occasional augmentations of fuel: the crucible should be kept covered as much as possible, which may be done with an iron plate or a cake of fire-clay. In a short time the whole fuses into a liquid with the evolution of gas. It should be kept in this state for ten or fifteen minutes, being occasionally stirred with an iron rod; the portion adhering to the rod should be examined from time to time, and when the liquid on it cools white, it is an indication that it is ready to be removed from the fire; but the first time a cast-iron crucible is used, this test will not be so accurate, the salt having then a light grey colour. When the crucible is removed from the fire, it should be placed upon a stone, the mass stirred, and then allowed to settle for a short time, after which the clear or liquid part is to be poured out upon a clean iron slab. The sediment should be scraped clean out of the crucible while it is hot, as the crucible will do to use again several times; but if the mass at bottom be allowed to cool, it will be difficult to remove it from the crucible afterwards. The clear liquid poured off is cyanide of potassium, having from 25 to 30 per cent. of cyanate of potash, and other impurities generally contained in commercial yellow prussiate of potash: 80 per cent. of cyanide of potassium is the greatest proportion that this process can give. We have occasionally obtained it at 78 per cent. from commercial materials, but more generally at 70 and 72 per cent.; and we have found cyanide of potassium in the market containing as little as 49 per cent. of pure cyanide.

The results of the manufacture of this salt on a large scale from the ordinary materials of commerce, shew that 55 lbs. of yellow prussiate, dried as directed above, yield 48 lbs.; and 19 lbs. of carbonate of potash give 18 lbs. of dry salts; in all 66 lbs. of the proper mixture.



Fig. 39.

The crucible used was of this shape (Fig. 39), capable of holding from two to three pints: in general two of them were used up in making the above quantity of cyanide, even when great care was taken. One great cause of the crucible giving way is the depth of the fire, and openness of the bars of the grate. The bottom of the crucible, between each pair of bars, fuses from the great heat concentrated near the opening.

To remedy this evil, a square tile of fire-clay should be laid upon the bars upon which the crucible is to rest. The tile must not cover all the bars, or the draught will be stopped—an equal space must be left at each side of the tile, which will preserve a regular heat around the crucible.

The quantity of clean cyanide of potassium obtained from the above quantity of materials was about 38 lbs.; the sediment scraped out of the crucible, being put into water, yielded about 6 lbs. more in solution, but of inferior quality—good enough, however, for precipitations, the cleaning of silver, and other general purposes in the factory.

It may be mentioned that in these operations the crucible is never allowed to cool, but as soon as the sediment is scraped out, it is again put into the furnace. If the iron sediment is not well cleared out, it imbibes oxygen rapidly, and the charge next taken from the crucible will have an excess of cyanate of potash, besides lessening the capacity of the crucible. Generally speaking, however, even when the utmost care is taken, the last charge has more cyanate of potash than the first. As a furnace for this operation is not always convenient, the electro-metallurgist can now be supplied in the ordinary market—cyanide of potassium being manufactured on a large scale, and sold at a price as low as an electro-metallurgist can make it for himself; however, all should be able to do so, and also to test the quality of what he may purchase. We have met with very inferior qualities in the market.

CYANIDE OF COPPER.—To prepare copper solutions by means of cyanide of potassium, for covering iron and other positive metals, there are several methods.

First Method.—To a solution of sulphate of copper add by degrees a solution of cyanide of potassium, which will give a yellowish-green precipitate, with slight effervescence. There will be evolved a gas, having a most pungent odour, to prevent the inhalation of which the most watchful carefulness has to be exercised, as it is very deleterious. It will be found that the copper is not all precipitated by the cyanide of potassium; for according to this mode, when a precipitate ceases to be formed, the solution remains greenish-blue, probably owing to the decomposition of the cyanate of potash and the formation of ammonia, which holds copper in solution, and forms also some complicated compounds with the cyanides of copper. If cyanide of potassium is added until the blue solution disappears, still copper is held in the solution, and may be detected by taking out a little, and adding to it a few drops of sulphuric acid, which will give a white precipitate of subcyanide of

copper. The loss of copper sustained is the only objection to this mode of preparing a copper solution. The cyanide of potassium is added until a precipitate is no longer formed; it is then allowed to settle, the clear liquid is poured off, and the vessel is filled with water: when the precipitate has again settled, the liquor is poured off, and this washing is repeated four or five times, in order to wash out the sulphate of potash which is formed during the precipitation. After being thus washed, a solution of cyanide of potassium is added to the precipitate until it dissolves. The coppering solution is now complete: it is of a light yellow colour, and is well adapted for ordinary purposes. The loss of copper is, however, considerable, being about one-fifth of the whole.

Second Method.—A coppering solution may also be prepared by adding to a solution of sulphate of copper a solution of carbonate of soda (washing soda will do), or carbonate of potash, which precipitates the copper as a green carbonate; continue adding the carbonate so long as a precipitate is produced, then put the whole upon a cloth filter. The precipitate is washed by filling up the filter several times with water—the liquid passing through the filter is allowed to run away. Put the filter, after the precipitate is washed, over a dish or the coppering bath, dissolve a quantity of cyanide of potassium in hot water, and pour this solution over the precipitate upon the filter, stirring it up the while. This will dissolve the precipitate, and the liquor passing through forms the coppering solution. The objections to this method is that it contains a great quantity of carbonate of potash or soda, formed from the mutual decomposition of the carbonate of copper and cyanide of potassium, and these carbonates deteriorate the solution.

Third Method.—The method we have adopted for manufacturing purposes is as follows:—To a solution of sulphate of copper we add a solution of ferrocyanide of potassium, so long as a precipitate continues to be formed: this is allowed to settle, and the clear liquor being decanted, the vessel is filled with water, and when the precipitate settles, the liquor is again decanted, and we continue to repeat these washings until the sulphate of potash is washed quite out. This is known by adding a little chloride of barium to a small quantity of the washings, and when there is no white precipitate formed by this test, the precipitate is sufficiently washed. A solution of cyanide of potassium is now added to this precipitate until it is dissolved, during which process the solution becomes warm by the chemical reaction that takes place. The solution is filtered and allowed to repose all night. If the solution of cyanide of potassium that is used is strong, the greater portion of the

ferrocyanide of potassium crystallises from the solution, and may be collected and preserved for use again. If the solution of cyanide of potassium used to dissolve the precipitate is dilute, it will be necessary to condense the liquor by evaporation, to obtain the yellow prussiate in crystals; the remaining solution is the coppering solution. Should it not be convenient to separate the yellow prussiate by crystallisation, the presence of that salt in the solution does not deteriorate it, nor interfere with its power of depositing copper.

PECULIARITIES IN WORKING CYANIDE OF COPPER SOLUTION.—The true composition of the salts thus formed by copper and cyanide of potassium has not yet been satisfactorily determined, being both various and complicated, also their relations to the battery and electrolysation are peculiar. The solution must be worked at a heat of not less than from 150° to 200° Fahr. All other solutions we have tried follow the laws laid down by Spencer and Smee, namely, that if the electricity is so strong as to cause gas to be evolved at the electrode, the metal will be deposited in a sandy or powdered state; but the solution of cyanide of copper and potassium is an exception to these laws, as there is no reguline deposit obtained unless gas is freely evolved from the surface of the article upon which the deposit is taking place. This necessitates the use of batteries of several pairs intensity, varying from five to nine pairs of Wollaston's battery, according to the heat and the state of the solution.

As this solution is used hot, a considerable evaporation takes place, which requires that additions be made to the solution from time to time. If water alone is used for this purpose, it will precipitate a great quantity of copper as a white powder, but this is prevented by dissolving a little cyanide of potassium in the water at the rate of about four ounces to the gallon; if the heat is maintained by steam this precaution is not required. The vessels used in factories for this solution are generally made of copper, which are heated over a fire, or on a sand bath—the vessel itself serving as the positive electrode of the battery; but any vessel will suit, but when the vessel is not of copper a copper electrode is employed.

PREPARATION OF IRON FOR COATING WITH COPPER.—When it is required to cover an iron article with copper, it is first steeped in hot caustic potash or soda, to remove any grease or oil. Being washed from that, it is placed for a short time in dilute sulphuric acid, consisting of about one part of acid to sixteen parts of water, which removes any oxide that may exist. It is then washed in water, and scoured with sand till the

surface is perfectly clean, and finally attached to the battery, and immersed in the cyanide solution. All this must be done with despatch, so as to prevent the iron from combining with oxygen. An immersion of five minutes' duration in the cyanide solution is sufficient to deposit upon the iron a film of copper. But it is necessary to the complete protection of the iron, if it has to be subjected to exposure to weather, that it should have a considerable thick coating: and as the cyanide process is expensive, it is preferable, when the iron has received a film of copper by the cyanide solution, to take it out, wash it in water containing a little cyanide of potassium, and then attach it to a single cell or weak battery, and put it into a solution of sulphate of copper. If there is any part not sufficiently covered with copper by the cyanide solution, the sulphate will make these parts of a dark colour, which a touch of the finger will remove. When this is the case, the article must be taken out, scoured, and put again into the cyanide solution till perfectly covered. A little practice will render this very easy. The sulphate solution for covering iron should be prepared by adding to it by degrees a little caustic soda, so long as the precipitate formed is re-dissolved. This neutralises a great portion of the sulphuric acid, and thus the iron is not so readily acted upon.

When the articles to be coated with copper are small in size the process is very easy; but when the surface is large, and when composed of cast iron, it is difficult to get every part of the iron coated, and requires a longer time in the cyanide solution. If the coated iron is not to be exposed to the weather, the coating in the cyanide solution will be enough. Of late, a large trade has been done in coppering cast-iron stands for paraffin and other lamps. The iron stand is cleaned as described, the coppering solution is kept at a boiling heat, a long deep bath is used, made of thick copper, which is attached to the copper of the battery; a thick brass rod is laid along the centre of the vat or bath, resting upon wood, and attached to the zinc of the battery—the battery is four pair of zinc and copper. The iron stands, when cleaned, are suspended in the solution by copper wire from this brass rod: in from seven to ten minutes they are completely covered with copper of a very rich golden colour, which they very soon lose by exposure. If the colour is to be retained, the article is washed in clean boiling water, so that it dries instantly on taking out; it is then coated over with thin copal varnish. Every kind of bronze tints can be got by exposure before varnishing. If a very dark bronze is required, they are exposed for some time before washing from the coppering solution. If a green colour is required, they are dipped in water containing a little ammonia or *salammoniac* in solution, and then exposed for some time. When

the desired tint is obtained the article is brushed with a hard hair brush, to bring out the coppery tint of bronze on the prominences, and then varnished with thin copal. We need hardly say here that this coating and bronzing can be applied with equal ease and usefulness to other castings than lamp stands—inside-stair railing, and any iron work not to be exposed to the weather can receive a coating of copper and be bronzed; but such a coating is quite unsuitable for iron to be exposed to the weather.

EFFECTS OF CONDUCTING POWER IN SOLUTIONS AND METALS.—In covering iron, platinum, or such comparatively bad conducting metals, with other metals that are good conductors, or the solutions of which are good conductors, the property of conduction in relation to the solution is beautifully illustrated. If we take a copper wire, say 8 or 10 feet long, one end of which is attached to the zinc of a battery, and laid parallel with the positive electrode into a solution for the purpose of receiving a deposit, it will be found that the greatest amount of deposit has taken place at the end farthest from the battery; but if an iron or platinum wire be substituted for the copper one, the contrary result will take place, for the end farthest from the battery will be the last to receive the coating, and will have the least quantity of metal deposited upon it. If the copper wire were 30 feet long, little alteration would be seen in the deposit; but upon an iron or platinum wire of that length the deposit proceeds only a certain distance, and no deposit will take place on the end farthest from the battery until the current has passed a considerable time, after which the deposit is observed to advance gradually. The copper as it becomes deposited on the iron acts as a conductor, transmitting the deposit farther onwards to its final point, as well as adding to the deposition already effected upon the iron. The length of deposit that would be formed on the first immersion of the wire depends upon the conducting power of the solution; for, as already stated, solutions vary in this property as well as metals. We have found that a few feet of iron wire offer a greater resistance to the passage of the current than a solution of cyanide of copper and potassium at a heat of 200° Fahr. which is only about three inches between the iron wire and the positive electrode; but their exact relations to each other we have not yet had an opportunity of investigating.

Under these circumstances, it may be asked, why not increase the intensity of the battery, and so force it along the wire? But this, as will be apparent, can only be done within certain limits; for, by increasing the intensity of the battery, it may be rendered too strong for the

solution near the battery, and thus a sandy deposit will be given at the one end and none at the other. The electro-metallurgist, when coating long lengths of iron wire with any metal, has to make connections with the battery every few feet. The wire is generally coiled up in the form of a corkscrew, and suspended by copper wires. We have found it very convenient to coil it upon a reel, having its armatures tipped with copper, which are connected with the battery. This plan insures a regular coating; but the position of the wire requires to be changed during the operation, otherwise the parts which press upon the arms of the reel will be left without deposit.

ILLUSTRATION OF CONDUCTION.—As an illustration of the effect of conduction between solutions and metal, we mention the following circumstance:—Having a large iron shaft, or rod, about 12 feet long and 3 inches average diameter, to cover with copper, we had it properly cleaned, placed in a hot solution of cyanide of copper and potassium, and surrounded by sheets of copper as a positive electrode. Two batteries of seven pairs intensity were attached, one at each end of the shaft; but by an oversight one of the batteries was not properly connected, the copper terminal of the battery having been attached to the shaft. Had the shaft been of copper, the one battery would have neutralised the other, so that there would not have been any deposit; or had the one battery been stronger than the other, there would have been a current and deposit equal to the excess of power of the one over the other. But, under the stated circumstances, a different result was obtained. After the batteries had been in action two hours, we found that a beautiful copper coating was imparted to that half of the shaft which extended from the point properly connected, while the other half was quite bare—no deposit having taken place upon it; but a deposit had been made upon the copper electrode opposite this non-affected half. The batteries did not, as we could perceive, affect one another, except that the one improperly connected prevented the deposit effected by the other proceeding farther than the half-length of the shaft; but it made the deposit obtained more perfect than would have been the case had there been only one battery at one end.

In this instance, the distance of the shaft from the electrode was 6 inches, so that the resistance of 6 feet of the iron was more than 6 inches of the solution: hence the influence of the contra-acting battery could not reach farther; or if any power passed farther it was neutralised by the other battery,—which we are inclined to think did not take place, *as the amount or thickness of deposit upon the one-half was fully more*

than we would have anticipated upon the whole, had the batteries been properly connected.

NON-ADHERENCE OF DEPOSIT.—Objections have been made to covering iron with copper for its protection, from an impression that the copper will not adhere to the iron; but if the operation is carefully performed the copper will adhere; when it does not, it will generally be found that it is the copper deposited from the sulphate which loosens from the copper deposited from the cyanide—occasioned, no doubt, by the article not having been sufficiently washed from the cyanide solution, and thus having a thin film of cyanide of copper precipitated upon the surface, which prevents the adhesion of the after deposit. Or, as it happens sometimes, that the cyanide of copper solution has not much free cyanide of potassium, and consequently, on putting the article into water, the cyanide of copper is decomposed by the water and precipitated upon the surface. If a little cyanide of potassium is dissolved in the first water used for washing out the depositing solution, this will be prevented (see page 100).

We have repeatedly deposited copper upon iron wire, and afterwards had it drawn out to twice its original length without the copper stripping off; but as the copper by this process becomes hard and brittle it is liable to break: the same takes place if the wire is much bent, and if it be made red hot, to anneal or soften the copper, it will oxidise, and if the coating is thin, the iron will be left bare in some places. We have known iron bolts, covered with copper, driven through 17-inch wood, and nails of all sizes subjected to rough work, without the deposit being injured. Some iron work coated with a thick coating in 1842, and exposed to the atmosphere, remained in good condition for twenty years. These remarks are also applicable to iron covered with zinc. The coating of iron with copper, for general exposure to weather, has been tried in a great variety of ways for large operations; but in general these trials have, commercially, ended unsuccessfully—the labour and cost is greater than the advantages sought will warrant for ordinary purposes. Many years ago trials were made to cover cast iron with copper, and then gild or plate for ornamental use, such as for outside railings, but without success. We give an abstract of a patent taken out for this purpose, shewing the desire for such work:—

COATING CAST IRON WITH OTHER METALS.

“Mr. W. Newton (for a correspondent) has patented the coating of cast iron permanently with copper, by depositing the copper by galvanic

action from a solution prepared by first taking a saturated solution of sulphate of copper in water and precipitating with carbonate of potash, and then re-dissolving in cyanide of potassium, whether the copper be deposited directly on the surface of the cast iron, or on zinc previously deposited thereon. The second part of this invention consists of coating cast iron with the alloy of copper called brass, by first coating the cast iron with copper or zinc, or both, and then depositing the brass thereon by galvanic action, from a solution formed by mixing with the solution of copper employed in the first part of the invention a solution of zinc prepared in substantially the same manner. The iron articles thus coated may be subsequently coated with gold or silver, so as to give them the appearance of these latter metals. The articles of cast iron to be coated or plated are first to be cleansed by what is known as the 'pickling' process with dilute sulphuric acid, and then 'scratch-brushed,' as it is termed, to free the surface from scale, sand, and other foreign substances which may not have been removed by the acid; and after this the castings are to be immersed in dilute nitro-muriatic acid. Any other mode of thoroughly cleansing the surface may be substituted for that above indicated. A solution of zinc is then prepared in the following manner:—Dissolve the sulphate of zinc in water until the water is saturated, and precipitate by means of prussiate of potash. The precipitate is then collected in a filter, and re-dissolved in cyanide of potassium. This constitutes solution number one. A solution of copper is then prepared in the same manner by dissolving sulphate of copper in water, and precipitating with carbonate of potash: this precipitate is dissolved in cyanide of potassium, and is called the second or copper solution. The third, or what may be termed the brass solution, is then prepared by mixing together the first or zinc solution with the second or copper solution, in such proportions as to produce the shade of colour required—increasing the proportional quantity of the one or the other at the discretion of the operator. The iron castings having been thoroughly cleansed, are first immersed in the first or zinc solution, and the galvanic battery applied in the usual manner of electrotyping, and continued until the required thickness of zinc is deposited on the surface of and caused to unite with the surface of the cast iron. The castings thus coated or plated with zinc are then to be immersed in the second or copper solution, and the galvanic battery applied as with the first or zinc solution, and continued until the required thickness of the copper shall have been deposited. In this way it will be found that the copper coating has become thoroughly *attached to the zinc*, and the zinc to the iron, so that they cannot be

removed except by filing or cutting, as in the case of a solid mass of copper; so that articles, of whatever form desired, which can be made of cast iron, can be coated with copper, so as to answer nearly if not all the purposes to which they could be applied if made of solid copper, thus greatly economising the cost. After the surface of cast iron has been coated with zinc or with copper, or with zinc and then with copper, which latter is much the best, if it be desired to coat it with brass, it is to be immersed in the third or brass solution, and the galvanic battery applied until the required thickness shall have been deposited. In doing this it is important that the positive pole of the battery should be made of brass, and as nearly as practicable of the shade of the brass to be deposited; for if a copper pole be applied, it will deposit in excess the copper portion of the solution. If desired the brass can be deposited on the coating of zinc instead of the coating of copper; but it will be found decidedly better to deposit the brass on the coating of copper, whether the copper be deposited directly on the cast iron or on a coating of zinc, although the latter is the best. In this way articles are produced having all the appearance, and answering nearly if not all the same purposes as if made entirely of brass, and at much less cost. The cast iron being thus coated with brass, the surface may be bronzed in the usual and well-known manner of bronzing brass; and as the process of bronzing on brass and copper is well-known, it will be unnecessary to give a detailed description of it. The surface of the cast iron being thus coated with brass, or with copper, can then be coated effectually with silver or gold in any of the well-known modes of coating brass or copper with those fine metals; it will not, however, be necessary to give the details of such mode or modes, as they are well known in the arts. The patentee remarks that it will be found better to deposit the silver or gold on the brass coating than on the copper coating, on account of the colour, particularly when, from reasons of economy, it is desired to make the coating of fine metal very thin. The patentee claims the process herein described, or any mere modification thereof, for coating cast iron with copper, by causing the copper, from a solution such as above described, to deposit by galvanic action, directly on the surface of the cast iron or on the zinc previously deposited thereon, as set forth. And also the process herein described, or any mere modification thereof, for coating cast iron with the alloy of copper known as brass, by causing the brass, from a solution such as above described, to deposit, by galvanic action, on to the surface of the cast iron, previously coated with zinc or copper, or both, as specified."

Whether this patented process was ever practically adopted by man-

facturers we do not know, but the deposition of zinc and copper together has been and is practised to a considerable extent by several manufacturers with differently prepared solutions. The following methods for making a brassing solution that works well is very simple: Dissolve together 2 lbs. sulphate of zinc and 2 lbs. sulphate of copper, and add to this a solution of carbonate of soda as long as a precipitate is formed; then wash this precipitate, as we have described for coppering solutions. Make two solutions of 4 lbs. of bisulphite of soda and 4 lbs. of cyanide of potassium. Put the precipitate into the solution of bisulphite of soda, and stir well; then add the solution of cyanide of potassium, which should render it of a lightish-yellow colour; filter the whole from any insoluble matter, and the solution is ready for use. A brass plate is to be used as an electrode. In working with this and every other brass or other alloy solution, great care is required for success, as the two salts have different conducting powers for the current; so that sometimes the copper is most deposited, at other times the zinc, according to the heat of solution or power of the current, which is shewn when depositing on large objects; the part next the electrode may be a good brass, while the parts farthest off will be of different tints; however, solutions generally improve by working; if the tendency is to give too much copper, more zinc has to be added, and if the tendency be to whiteness, add more copper to the solution. Such deposits are mostly used for coating small objects which are not to be exposed to the weather. In a paper read before the British Association in 1870, by W. H. Waleren, F.C.S., "Upon the Deposition of Brass," the author says, "Ordinarily a solution containing the cyanide of copper and zinc respectively, dissolved in a solvent solution consisting of a mixture of potassic cyanide with a salt of ammonium, is employed to deposit brass. This solution, however, evolves hydrogen copiously, and is only workable by means of two Grove's cells. The evolution of gas may be either totally stopped or much lessened by dissolving as much of the metallic cyanides as the solution will take up, and then further charging the solution with the copper and zinc oxides. The evolution of gas may be totally stopped by the further use of cupric ammonide. When the evolution of hydrogen is stopped, a single Smee's cell is sufficient to deposit the alloy; but in practice a single Grove's cell or equivalent magnet electro-power is employed in order to shorten the time of immersion in the electro-coating bath." The quality or colour of the brass (yellow or red) depends upon the heat of the solution. This process is strongly recommended for giving cast iron used for architectural purposes the appearance of brass.

COATING OF IRON WITH ZINC.

In covering iron with zinc, the precautions necessary for copper are not required: zinc being positive to iron, acids have a stronger affinity for it than for iron, and therefore a solution of an acid salt may be used. The one generally used is the sulphate.

SULPHATE OF ZINC.—Zinc dissolves easily in sulphuric acid, and the solution by evaporation yields crystals of sulphate of zinc; but as the salt is very cheap and abundant in the market, it is more convenient and economical to buy than to make it. The solution for depositing is made by dissolving two pounds of the crystallised salt in one gallon of water. The single-cell process cannot be used advantageously with this solution. A separate battery is necessary and a zinc positive electrode. The metal is very easily deposited—one or two pairs of Wollaston's battery being sufficient for coating small articles.

Zinc may be deposited upon blacklead surfaces in the same manner as copper; but unless more than ordinary precautions are observed, an article formed in this manner is so brittle that it can hardly be handled without breaking from its crystalline character. When the deposition upon blacklead is attempted, the best method is to have the solution saturated with the salt, employing a battery of six or seven pairs of plates, and keeping the article on which the deposit is forming constantly in motion.

The use of cyanide of zinc has been recommended, but for what good reason it is hard to know. In several trials we made there were presented great practical difficulties. The positive electrode became coated, after a few minutes' working, with a white pasty matter, which prevented further action, and all but stopped the current. Some of this white coating collected, washed, and dried in the air, gave by analysis—

Oxide of zinc,	51·3
Cyanogen,	1·7
Iron,	trace
Potash,	2·3
Carbonic acid,	27·8
Matter insoluble in HCl,	2·5
Water,	14·8

 100·4

The zinc appears to be converted into carbonate of zinc, and deposits on the pole; the potash combines with the cyanogen as cyanide of potassium, and surrounds the article getting the deposited metal.

USE OF ZINC COATING.—The principal application of zinc is upon iron, to protect it from corrosion, which it does, not only as a coating, but from its more electro-positive character it protects it by a galvanic influence. The voltaic influence of zinc for protecting iron is a subject that has occupied the attention of practical men for a long time: it is one of high importance: nevertheless, there seems yet a great deficiency in our knowledge of the extent of this influence, and how and when it is effective.

Upon this subject the late Professor Faraday, in the *Report of the Harbours of Refuge Commissioners*, states, "Zincd iron would no doubt resist the action of sea-water so long as the surface was covered with zinc, or even when partially denuded of that metal; but zinc dissolves rapidly in sea-water, and after it is gone the iron would follow.

"As to voltaic protection, it has often struck me that the cast-iron piles proposed for lighthouses or beacons might be protected by zinc in the same manner as Davy proposed to protect copper by iron; but there is no doubt the corrosion of the zinc would be rapid. If not found too expensive, the object would be to apply the zinc protectors in a place where they could be examined often, and replaced when rendered ineffective. In this manner I have little doubt that iron would be protected in sea-water."

INFLUENCE OF GALVANISM IN PROTECTING METALS FROM DESTRUCTION BY OXIDATION AND SOLUTION.

The galvanic influence of one metal in protecting another is in relation to their negative and positive qualities in the circumstances they are placed together with their conducting powers. Their relations in sea-water are silver, copper, bismuth, antimony, iron, tin, lead, cadmium, zinc; the first the most negative, the last the most positive in the series. So that, according to this scale, the farther apart the metals may be which are selected for experiment, the more decided will be the power of the positive to protect the negative. Copper and zinc operate more strongly together than iron and zinc.

A metal that is insoluble when placed singly in a fluid may be made soluble by connection with a relatively negative metal placed in the same fluid. For example, pure zinc put into muriatic acid is unaffected, but when connected with copper in the same fluid it is rapidly

acted upon. Or a metal may be soluble in a fluid alone, but may be rendered insoluble by connection with a relatively positive metal, which undergoes decomposition instead. Thus, copper is dissolved in sea-water when alone, but when a piece of zinc is connected with it, the copper is unaffected. This last effect is the substance of Davy's method of protection alluded to by Dr. Faraday. In applying this principle, it is necessary to take into consideration—

1st, The amount and power of electricity generated by the connected metals in the same fluid; and

2nd, The conducting power of the metal which is being protected.

1st. The amount and power of the electricity evolved is in proportion to the difference of the relative negative and positive conditions of the metals employed. The more negative the coated metal or metal being protected is, the less it requires protection, although its powers of giving protection are the greatest. And the more positive the coated metal the more liable it is to be destroyed, and the greater the amount of electricity required to protect it; but unfortunately it is less able to generate this electricity when in contact with another metal. Thus these two conditions are opposed to the application of galvanic influence for protecting iron.

Suppose, for example, that 4 square inches of zinc in connection with 4 square feet of copper, give out sufficient electricity to protect the copper from sea-water, it will be found that to obtain the same amount of electricity by iron and zinc, 2 square feet of the latter to 4 square feet of the former are required.* Besides this, the same quantity of electricity that protects copper will not protect iron; nor will any quantity of zinc protect iron from corrosion in sea-water—even a bar of iron placed in a zinc vessel filled with sea-water is not completely protected.

2nd. The conducting power of the negative or protected metal subjected to submarine immersion is a subject of very great importance. Suppose a piece of copper and a piece of zinc be connected under a solution—say a copper bar (c) 4 feet long, with a piece of zinc

(z) 4 inches in length, erected on one end, as in the annexed sketch:—

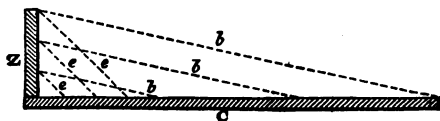


Fig. 41.

The conducting power of the copper is so much superior to that of the solution that the

* These proportions, given in round numbers, are nearly accurate; but they vary according to the kind of iron, the state of the water, the distance of the metals, &c.

whole length of the bar will become instantly negative, and the current of electricity will pass to and from all parts of the bar at the same time in the lines *b, b, b*; but the current will be more active towards the point of contact than towards the distant extremity—the resistance of the solution being less in proportion to the proximity of the metals. But if a bar of iron, and a piece of zinc as a protector, be placed in the same circumstances, the phenomena assume quite a different aspect: the conducting power of iron being much less than that of copper, the distant extremity will not be affected by the electric current, which will find a more easy passage, as indicated by the dotted lines *e, e, e*, beyond which the electric effort ceases; and even in that portion of the bar which is under the influence of the current, the part nearest the zinc is better defended than those parts which are farther distant. This partial protection, while it induces a negative state at the near end, renders the other end more positive. Such a diversity of condition gives rise to voltaic action between the two extremities of the bar *c*, and the result is the destruction of the far end. In all cases of voltaic protection the more equal the influence over the whole surface protected, the more perfect is the protection. An inequality of protection, such as we have described, is productive of numerous evils. It is, we believe, the source of many of the injuries occurring in our day to copper sheathing. One part of a sheet becoming, by some local cause, negative, the other parts are thus rendered positive; the result is, that upon the borders of an individual sheet either overlapping or underlying its neighbouring sheet, an electric current is excited, passing through the stratum of moisture which may intervene, and the ultimate effect is, that the positive edge is dissolved as effectually as if cut by a knife. The evil arising in one place may be so contagious as to affect a whole neighbourhood—sometimes the whole side of a ship's bottom.

In fresh water, iron covered with zinc cannot be protected any length of time, for the zinc coating speedily oxidises and comes off and exposes the iron. When iron is simply exposed to the air, a good coating of zinc is a sure protection. We have seen iron of various qualities coated by the electro process and exposed to the atmosphere, in all weathers, for several years, without being more affected than a piece of zinc would be. In spots where abrasion has taken place by accident or otherwise, the protecting power of the zinc is nil, and the iron rusts as if there were no zinc present. No other result, however, could be anticipated, as there can be no electric excitation without a liquid to connect the two metals.

In the early days of electro-metallurgy the tinplate manufacturer saw in the practice what might revolutionise his trade. Tin was costly, zinc was cheap; tin was electro-negative to iron, and hastened its destruction when any part of the iron was exposed. Zinc was electro-positive to iron, and would consequently protect it from corrosion as long as any coating remained. Such were the prevalent and popular ideas upon this matter; and to put these to the test we were invited to several large tinplate works, to the first of which we went with the most sanguine prospects, which were given up after a few days' trial; but it required experience to shew the inefficiency of the electro-process to compete with the tinning, not only that the coating of zinc given to the iron by the battery was no proper protection, but the depositing of this coating requiring several hours was as expensive as tin; and to do the quantity required in the trade would require acres for erection of vats and batteries.

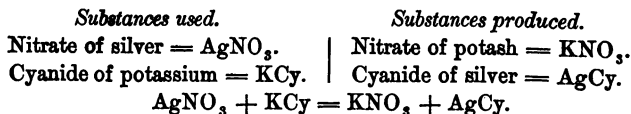
The iron to be coated by zinc is to be cleaned and prepared in the same manner as we have described for the purpose of covering it with copper (page 119).

ELECTRO-PLATING.

THE next applications of the electro-deposition we have to notice are those relating to silver and gold, embracing the arts of electro-plating and gilding—arts which have revolutionised some extensive branches of manufacture effecting the same object but by different means.

TO MAKE SILVER SOLUTION.—The solution of silver used for plating consists of cyanide of silver dissolved in cyanide of potassium, which may be prepared in various ways. We shall first describe some of the preparations most in use, and also point out practical objections which, in special cases, have occurred under our own observation, not omitting to specify and recommend those methods which have approved themselves to us as being most simple and effective.

The method generally adopted is as follows:—Metallic silver is dissolved in four parts of nitric acid, diluted with one part of water: the diluted acid is heated by putting the vessel in hot water or on a hot plate, the silver is added by degrees. The operator must avoid breathing the fumes which ascend, as they are highly deleterious. The metal being dissolved, the solution is transferred to a large vessel, and diluted with water. To this is added a solution of cyanide of potassium so long as a white precipitate is formed. This precipitate is cyanide of silver, and the action which ensues may be thus represented—



The propriety of diluting the nitrate of silver before precipitating by the cyanide of potassium arises from the fact, that the salts of potash and soda (such as the nitrates, chlorides, and sulphates), when in strong solution, dissolve small quantities of the silver salt, and thus cause a loss, which is prevented by previous dilution with water.

When the precipitate of cyanide of silver has settled, the clear solution is carefully decanted, and the vessel filled up with water, which is again decanted as soon as the precipitate has settled. This process is to be repeated three or four times, so as effectually to wash out the soluble salts. When properly washed, a solution of cyanide of potassium is added to the precipitate, until it is all dissolved. The resulting solution is cyanide of silver, dissolved in cyanide of potassium, and forms the plating solution. It ought to be filtered previous to using, as there is always formed a black sediment, composed of iron, silver, and cyanogen, which, if left in the solution, would fall upon the surface of the article receiving the deposit, and make it rough. The sediment, however, must not be thrown away, as it contains silver. The cyanide of potassium, used to dissolve the cyanide of silver, may be so diluted that the plating solution, when formed, shall contain one ounce of silver in the gallon: of course, the proportion of silver may be larger or smaller, but that given is what we consider good for plating.

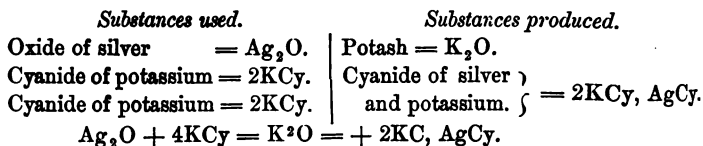
In dissolving 100 ounces of silver, the following proportions of each ingredient are those which we have found in practice to be the best. Take 7 pounds of the best nitric acid* and 61 ounces of cyanide of potassium, of the average quality described at page 115: this quantity will precipitate the 100 ounces of silver dissolved in the acid solution. After this is washed, take 62 ounces more of cyanide of potassium, the solution of which will dissolve the precipitate: this being done, the plating solution is then formed. Of course, these proportions will vary according to the difference in the quality of the materials; but they will serve to give an idea of the cost of the silver solution prepared in this manner.

In making up a solution in this way, great care is necessary in the precipitation of the silver from the nitrate. If there is not a sufficiency of cyanide of potassium added some silver will remain in solution. Again, should there be a slight portion more added than is required, some of the precipitate is dissolved, so that in either case there is a loss of silver. It is safest in making up a solution by this method, to keep the first liquor that is decanted off; and if a large quantity of silver is being operated upon, keep also the second decantings, and add to these a little hydrochloric acid, which will precipitate any silver present as a chloride, which can be collected upon a filter and reduced by means which will be given afterwards.

* The nitric acid must be free from hydrochloric (muriatic) acid: to a small quantity of the acid, in distilled water, add a few drops of solution of nitrate of silver; if it gives a milky white precipitate, it contains muriatic acid, and should be rejected.

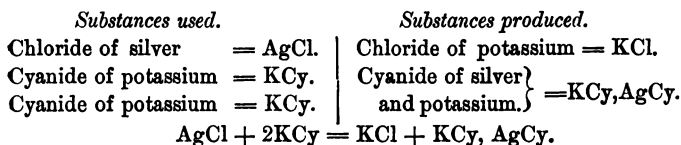
CYANIDE OF SILVER DISSOLVED IN YELLOW PRUSSATE OF POTASH.—We have occasionally dissolved the cyanide of silver by yellow prussiate of potash, three pounds of which are required to dissolve one ounce of silver. This forms an excellent plating solution, and yields a beautiful surface of silver. It must have a weak battery power, and consequently the silver is very soft. The positive electrode does not dissolve in this solution: there is formed upon its surface a white scaly crust, which drops off and falls to the bottom; and the solution soon becomes exhausted of silver, and is not of practical use.

SOLUTION MADE WITH OXIDE OF SILVER.—Oxide of silver may be formed in different ways, but the most simple is adding to a solution of nitrate of silver a solution of caustic, potash, or soda, which precipitates the silver as an oxide. This precipitated oxide is washed by decanting, as we have described in making cyanide of silver. By dissolving this oxide of silver in cyanide of potassium it forms a solution of cyanide of potassium and silver; but this preparation is less economical, because the materials used in converting the silver into an oxide are lost; it requires the same amount of cyanide of potassium as the process just described, and brings, moreover, an equivalent of potash into the solution, which is a disadvantage. The following diagram shews the reactions that occur:—



SOLUTION MADE WITH CHLORIDE OF SILVER.—The nitrate of silver may also be precipitated by adding a solution of common salt to it, and treating it in the same way as described for precipitation by cyanide of potassium: this would form chloride of silver, which may be dissolved in cyanide of potassium, thus forming the silver solution. But the objection urged against the use of oxide of silver is equally applicable in the case of chloride; and great care is required in precipitating large quantities and strong solutions of silver by common salt, the chloride of silver being soluble in the salts of the alkalies—such as the nitrates, chlorides, and sulphates, and there is therefore great liability to loss by this process, and we have not the redeeming quality of a saving. By *precipitating* afterwards from the decanted liquor with hydrochloric

acid, the best means of recovering any silver thus dissolved is dilution, as the chloride is barely soluble in dilute solutions of the above named salts. In making a plating solution by this means, put all the decanted liquors together, and allow them to stand for several hours, when any chloride of silver dissolved will fall to the bottom of the vessel and can be recovered. The reaction which takes place by dissolving chloride of silver in cyanide of potassium may be illustrated as follows:—



Thus, we observe, that the action taking place is not mere solution but decomposition; which upon 100 ounces of silver in this preparation produces an impurity of 70 ounces of chloride of potassium, which, although not injurious to the working of the solution, would nevertheless be much better away.

THE BEST METHOD OF MAKING SILVER SOLUTION.—The best and cheapest method of making up the silver solution is by the battery, which saves all expense of acids and the labour of precipitation and washing. This is effected by taking advantage of the principle of non-transfer of the metal in electrolytes (see page 90). To prepare a silver solution which is intended to have an ounce of silver to the gallon (see page 133), observe the following directions:—Dissolve 123 ounces of cyanide of potassium in 100 gallons of water; get one or two flat porous vessels, and place them in this solution, leaving out half an inch of the mouth of the porous cell, and fill them with the same solution to the same height as the solution outside; in these porous vessels place small plates or sheets of iron or copper, and connect them with the zinc terminal of a battery: in the large solution place a sheet or sheets of silver connected with the copper terminal of the battery. This arrangement being made at night, and the power employed being two of Wollaston's batteries, of five pairs of plates, the zincs 7 inches square, it will be found in the morning that there will be dissolved from 60 to 80 ounces of silver from the sheets. The solution is now ready for use; and by observing that the articles to be plated have less surface than the silver plate forming the positive electrode for the first two or three days, the solution will then have the proper quantity of silver

in it. We have occasionally found a little silver in the porous cell: it is therefore not advisable to throw away the solution in them without first testing it for silver, which is done by adding a little muriatic acid to it.

From this description the amateur electrotypist may easily make up a small quantity of solution for silvering his medals or figures: half-ounce of silver to the gallon of solution will do very well for his purpose: a small quantity of solution may be prepared in little more than an hour.

As the cyanide of potassium dissolves silver without the aid of a battery, by merely allowing some silver scraps or silver to steep in this solution for a few days, a plating liquor may be formed; but this is tedious and uncertain, although for small operations, and where porous vessels are not convenient, it will serve the purpose.

Other solutions of silver besides the cyanide may be employed, if the law stated at page 114 is strictly observed. Indeed, every salt of silver has not only been tried, but is either the subject of a patent, or prominently included in it. None of them, however, with the exception of two, have we found of any practical value compared with that already described: these are the chloride of silver dissolved in hyposulphite of soda, and the sulphite of silver dissolved in sulphite of potash, or sulphite of soda, which are prepared as follows:—

HYPOSULPHITE OF SILVER SOLUTION.—The simplest method known to us for forming the hyposulphite of silver solution is this:—Take one pound of pure carbonate of soda, well dried, as described at page 115; mix it intimately with five ounces of flowers of sulphur; place the mixture over a slow fire without flame, in a porcelain or stoneware basin, which must be supported by an iron trellis, or any convenient support, to prevent it touching the red coal; keep the mixture constantly stirred, and maintain the heat till the sulphur melts, and the mass inclines to get pasty and rough: while in this state, keep stirring for about fifteen minutes, in order to bring every part in contact with the air. Set the mixture to cool, after which dissolve it in water: boil the solution for some time, adding sulphur; then filter it, and allow it to evaporate at a slow heat: the crystals formed are hyposulphite of soda.

This salt is manufactured on a large scale, and can be purchased in the market in a crystalline form, and which we would recommend in preference to making it.

To prepare the silver solution, the silver is first dissolved in nitric acid, and then precipitated by a solution of common salt, and washed, with the precautions stated at page 134. When the precipitated

chloride of silver is well washed, some of the crystals of hyposulphite of soda are dissolved, and the solution is added to the chloride of silver, which it dissolves, forming the plating solution. If the operator makes the hyposulphite, it is not necessary to crystallise the hyposulphite of soda; it should be used as soon as made.

The hyposulphite of silver solution is very easily decomposed by the electric current, so that a weak battery will suffice to plate by it; but the great objection is its liability to decompose in the light, and to deposit the silver as sulphide: unless great care is exercised, the silver deposited from it will be in a granular condition, which is a great objection in plating.

SULPHITE OF SILVER PLATING SOLUTION.—The sulphite of silver solution is prepared in the following manner, as described by the patentee of the process:—

“The solution which I use is made in the following manner:—I take of the best pearl-ash of commerce 28 lbs. (avoirdupois), and add to it 30 lbs. (avoirdupois) of water, and boil them in an iron vessel until the pearl-ash is dissolved; the solution should then be poured into an earthenware or other suitable vessel, and suffered to stand until the liquor becomes cold. It should then be filtered, and 14 lbs. (avoirdupois) of distilled water added thereto; sulphurous acid gas (obtained by any of the known processes) should then be passed into the filtered liquor until it is saturated, taking care not to add sulphurous acid gas in excess. The liquor should be again filtered, and the liquor so filtered is what I term the solvent or sulphite of potash.

“To make the silvering liquor which I use in coating with silver, the surface of articles formed of metal or metallic alloys, I dissolve 12 ounces (avoirdupois) of crystallised nitrate of silver in 3 lbs. of distilled water (in a clean earthenware vessel), and add to the solution, by a little at a time, the beforementioned solvent, so long as a whitish coloured precipitate is produced (care being taken not to add more of the solvent than is necessary). After the precipitate has subsided, I pour off the supernatant liquor, and

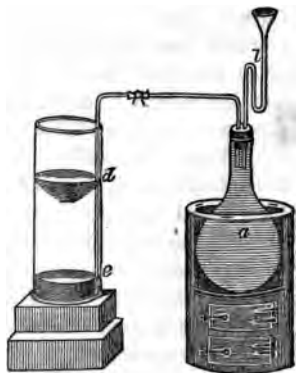


Fig. 41.

wash the precipitate with distilled water. To the precipitate I add as much of the before-mentioned solvent as will dissolve it, and afterwards add about one-sixth part more of the solvent, so that the solvent may be in excess; I then stir them well together, and let them remain about twenty-four hours, and then filter the solution, when it will be ready for use. This is what I designate Silvering Liquor.”*

Sulphurous acid gas for making the above liquor may be prepared by heating sulphuric acid, undiluted, in a flask or any convenient vessel, adding small pieces of copper or charcoal: the gas escaping is made to pass into the solution to be saturated with it.

Fig. 41 is a very convenient apparatus for the preparation of this gas for saturating solutions.

This solution is also very easily decomposed by the electric current, and serves the purposes of plating very well; but it is also liable to decomposition by light, and is not so good in practice as the solution of cyanide of potassium and silver. The latter solution is, however, also liable to a kind of decomposition, by long exposure, not yet fully investigated, but it is wholly confined to the impurities in the cyanide of potassium, which never deposits silver; whereas the decomposition that takes place in the sulphite or hyposulphite affects the silver compound, and precipitates the silver from solution.

TO RECOVER SILVER FROM SOLUTION.—When a silvering solution, no matter how made, gets out of order, and cannot be rendered fit for use again, the silver may be recovered by adding to the solution any acid that will neutralise the alkali; the best is hydrochloric acid, when the silver will be precipitated as a chloride, in which case the solution should be diluted, or a portion of the precipitate will be redissolved (see page 134). The precipitate is allowed to deposit, the clear liquor decanted, and the vessel filled with water to wash the precipitate, which is afterwards collected upon a filter and dried, and then mixed with twice its weight of carbonate of potash, and fused in a Hessian crucible for fifteen minutes, or until the fused fluid ceases to effervesce. On removing the crucible, and pouring the whole into an iron ladle, the silver will be found, when cool, in the metallic state at the bottom of the ladle.

In these operations, when pouring the acid into a cyanide solution, great care must be taken not to inhale the fumes given off, which are very abundant, sickening, and poisonous. (See effects of breathing cyanogen on health.) The operation should be done in the open

* *Reperitory of Patent Inventions*, Fifth Series, page 210, 1843.

air, and even then it is dangerous. Instead of throwing down the silver by an acid, it is better to evaporate the solution to dryness, and to fuse the product as described, in which case the cyanide of potassium present is an excellent reducing flux, requiring no addition of carbonate of potash, and saves the necessity of evolving poisonous fumes.

When this last method is adopted, and the solution has contained yellow prussiate of potash, it is found that during this fusion portions of the metal sometimes form a scoriaceous nodule at the bottom of the crucible, and all the heat that can be applied by an ordinary assay furnace will not fuse it. This refractory piece, when cooled, has generally a rough scoriaceous surface, and is exceedingly hard. When filed it has more the colour of German silver than of real silver; it has considerable malleability, and retains its bright appearance for a long time without tarnish. An analysis of this alloy gave—

Silver,	82.15
Copper,	9.12
Iron,	7.50
Carbonaceous matter,	46
								99.23

If we suppose the carbonaceous matter to be an accidental impurity, this alloy will nearly agree with the formula Ag_6CuFe .

PREPARATION OF ARTICLES FOR PLATING.—Articles that are to be plated are first boiled in an alkaline ley, to free them from grease, then washed from the ley, and dipped into dilute nitric acid, which removes any oxide that may be formed upon the surface; they are afterwards brushed over with a hard brush and sand, of which a kind obtained from the Isle of Wight, and known as silver sand, is the best. The alkaline ley should be in a caustic state, which is easily effected by boiling the carbonated alkali, and adding slaked lime, until, on the addition of a little acid to a small drop of the solution diluted with cold water, no effervescence occurs. The lime is then allowed to settle, and the clear liquor is fit for use. The ley should have about half a pound of soda-ash, or pearl-ash, to the gallon of water. The nitric acid, into which the article is dipped, may be diluted to such an extent that it will merely act upon the metal. Any old waste acid will do for this purpose. In large factories the acid used for dipping before plating is generally afterwards employed for the above purpose of cleaning.

The article being thoroughly cleaned and dried is weighed, and a copper wire attached to it, either by twisting it round the article or putting it through any open part of it, to maintain it in suspension. It is then dipped into strong nitric acid as quickly as possible, washed through water, and then immersed in the silver solution, suspending it by the wire upon a brass rod which crosses the mouth of the vessel and is attached to the zinc of the battery. The nitric acid generally used and found best for dipping has a specific gravity of 1.518, and contains 10 per cent. sulphuric acid, and costs about 3d. per pound. The article is instantaneously coated with silver, and ought to be taken out after a few seconds and well brushed. On a large scale, brushes of brass wire attached to a lath are used for this purpose; but a hard hair brush with a little fine sand will do for small work. This brushing is used in case any particle of foreign matter may be still on the surface. It is then replaced in the solution, and allowed to remain till it receives the proper coating; in the course of a few hours a coating of the thickness of tissue-paper is deposited on it, having a beautiful matted appearance of dead silver. If it is desired to preserve the surface in this condition, the article must be taken out, care being taken not to touch it by the hand, and immersed in boiling distilled water for a few minutes. On being withdrawn, sufficient heat has been imparted to the metal to cause it to dry instantly. If it is a medal, it ought to be put in an air-tight frame immediately, or if a figure, it may be at once placed under a glass shade, as a very few days' exposure to the air tarnishes it, by the formation of sulphide of silver, and that more especially in a room where there is fire or gas. If the article is not wanted to have a *dead* surface, it is brushed with a wire brush and old ale, beer, or water containing in solution a little gum, glue, or sugar; but the amateur may use a hard hair brush. It may be afterwards burnished, according to the usual method of burnishing, by rubbing the surface with considerable pressure with ordinary burnishing tools of polished steel, or the mineral termed *bloodstone*,—brown oxide of iron.

We may remark, that in depositing silver from the solution a weak battery may be used; though when the battery is weak the silver deposited is soft, but if used as strong as the solution will allow without escape of gas, say eight or nine pairs, the silver will be equal in hardness to rolled or hammered silver. If the battery is stronger than the solution will stand, or the article very small compared to the size of the plate of silver forming the positive electrode, the silver will be deposited as a powder. The average cost of depositing silver in this way, using three pairs of zinc and copper, is 2d. per ounce. Gas should never be seen

escaping from either pole; and the surface of the article should always correspond as nearly as possible with that of the positive electrode, otherwise the deposit runs the risk of not being good; it requires more care, and the solution is apt to be altered in strength, because if the positive electrode be large compared with the negative, the solution will become stronger in silver, while if smaller in proportion, the solution will become exhausted of silver.

In plating large articles, especially old articles being replated, as well as new articles with large surface, it is not always sufficient to dip them in nitric acid; wash and immerse them in the solution, in order to effect a perfect adhesion of the two metals, there being a tendency, in the time required, to slight oxidation. To secure perfect adhesion, a small portion of quicksilver is dissolved in nitric acid, and a little of this solution is added to water, in sufficient quantity to enable it to give a white silvery tint to a piece of copper when dipped into it: the article then, whether made of copper, brass, or German silver, is, after being dipped in the nitric acid and washed, dipped into the nitrate of mercury solution till the surface is white: it is then well washed by plunging it into two separate vessels containing clean water, and finally put into the plating solution. One ounce of quicksilver thus dissolved will do for a long time, though the liquor is used every day. When the mercury in this solution is exhausted, it is liable to turn the article black upon being dipped into it. This must be avoided, as it causes the deposited metal to strip off; the only remedy is a new solution of mercury.

PRACTICAL INSTRUCTIONS IN PLATING.—We need hardly add that it is necessary the battery should be so arranged, that the *quantity* of electricity generated should correspond with the surface of the articles to be coated, and that the *intensity* should be regulated according to the state of the solutions; that is to say, that the *quantity* should be sufficient to give the required coating of metal in a given time, and the *intensity* such as to cause the electricity to pass easily through the solution to the articles. It is also essential for regular working, as stated above, that the plates of metal forming the positive pole in the solution should be of corresponding surface to the articles to be coated, and should face them on both sides.

The following is the arrangements which were for a long time adopted in some of the large plating manufactories:—The *vat*, or plating vessel, measured about $6\frac{1}{2}$ feet in length, by 33 inches in breadth, and 33 inches in depth, and generally contained from 200 to 250 gallons of solution;

the silver plates, serving as electrodes, were nailed upon frames of wood, but are now generally fixed upon light iron frames, these not being affected by the solution: two battery troughs were arranged, as seen in Fig. 42, consisting of six batteries of three pairs intensity. The zinc plates immersed in the acid measured 6 inches by 7 inches, the exposed surfaces of which measured 84 square inches: these multiplied by 6 give 504 square inches, from which electricity was disengaged. The surface of the silver electrodes exposed and opposed to the articles receiving the deposit varied from 3000 to 4000 square inches of surface, which was generally in excess of the surface of the articles being plated, and consequently the solution had the tendency to become stronger in silver.

The following figure, with explanations, will illustrate these observations:—

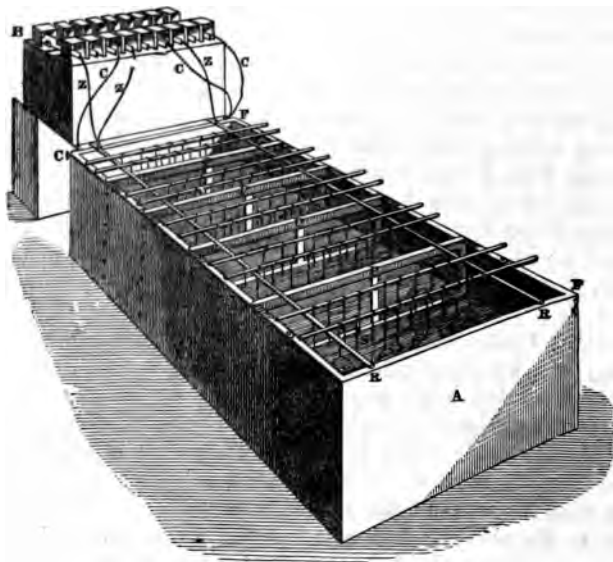


Fig. 42.

A, vat or vessel containing the solution; B, batteries with zinc, the poles, ZZ, connected with rods, RR; and the copper poles, CC, connected with the metallic sheets, PP, in the solution, by means of the copper slip, FF; DD, are articles suspended in the solution by wires from the rods, RR; S, the solution. So soon as the articles which are connected

with the negative pole of the battery, and the metallic sheets connected with the positive pole, are both immersed in the solution, the galvanic circuit is completed.

In most plating establishments the batteries are now placed outside the house, and the connecting rods are brought from them into the vats, so as to preserve the workmen from the injury arising from inhaling the hydrogen gas which is given off by the zincs, as it often contains arsenic, and hence is highly injurious to health; the gas of the battery has a strong effect upon the nostril, exciting dryness with pain. Wherever the batteries are placed, they should not be exposed to cold, as their operation is much affected by the temperature.

In the early days of electro-plating the batteries used were round. They consisted of a copper cylindrical vessel, about 20 inches deep, and 5 inches diameter, filled with dilute sulphuric acid. A piece of wood was placed at the bottom of this vessel, and a cylinder of zinc, the same depth as the copper vessel, and about 3 inches diameter, was placed inside the copper vessel. A wooden ring, floating on the surface of the acid, prevented the zinc and copper touching—a binding screw was attached to each, and formed a battery of a single pair. Six batteries of this size were connected with such a vat as is described above. The test of strength employed to determine whether the working power was sufficient was that, when connected with an electro-magnet, it should support a 7 lb. weight. We believe that many platers and gilders still use such batteries, and that when the solutions and apparatus are all in good condition they do well. They are, however, far from being so economical as the battery with square plates shewn above. Most electro-metallurgists now use large and deep stoneware vessels, in which are placed the zinc and copper—the plates having several square feet of surface; four pairs of such arranged for intensity is common. We have already shewn, when treating of batteries, that very large plates are not consistent with economy.

To ascertain the amount of metal deposited, it is necessary to weigh the articles carefully before and after plating. But between the first weighing and the immersion of the articles in the plating solution there is the dipping into nitric acid to be accounted for: this on an average will cause a loss of about 1 pennyweight upon an article of the size of a foot square; thus, if a waiter of a foot square, made of copper or German silver, shews, when coated, a difference in weight of 19 pennyweights, the silver laid on must be estimated at an ounce, or 20 pennyweights. When the article is a "replate"—i.e., an old plated article that has become bare of silver in parts—the allowance or reduction for

the dipping in the acid is only to include the portions left bare, for the silvered parts are not acted upon by it. One of the practical difficulties which the inexperienced will occasionally meet with when a "replate" is dipped in the nitric acid is, that a galvanic action is produced between the silver and the copper portions, which causes a black line round the edge of the silver: this ought immediately to be rubbed off, but even with rapid and careful rubbing there is great risk that the coating will loosen and blister at those parts; and besides this, it happens that the parts of the "replate" which are sound, the silver not being acted upon by the acid, but rather protected by the galvanic action, are not in a fit state to receive and maintain a perfect adhesion of the deposit, and therefore the risk is great that the new coating will separate from the old, or, in technical language, that the part will *strip*. Under these circumstances, experience has taught that the best way to proceed is to take all the old silver off the article, and deposit an entirely new coating.

There are two methods of taking off the silver:—

TAKING SILVER FROM COPPER, &c.—First, stripping or dissolving it off: this is done by putting into a stoneware or copper pan some strong sulphuric acid (vitriol), to which a little nitrate of potash is added: the article is laid into this solution, which will dissolve the silver without materially affecting the copper; saltpetre is added by degrees, as occasion requires; and if the action is slow a little heat is applied to the vessel. The silver being removed, the article is washed well, and then passed through the potash solution, and finished for plating. When the sulphuric acid becomes saturated with silver it is diluted, and the silver is precipitated by a solution of common salt: the chloride of silver formed is collected and fused in a crucible with carbonate of potash, when the silver is obtained in a metallic state, as a knob or button (see page 138). The crucible should not be over two-thirds full, and should be kept in fusion till effervescence ceases, if the whole precipitate is used. The crucible is removed from the fire, and when cool it is broken.

The article thus stripped by acids often shews a little roughness, not from the effects of the acid, but because the copper under the silver had not been polished. The silver and copper upon old plated goods have had their surfaces fused together, so that when the silver is dissolved off the copper surface is of necessity rough. It is therefore a necessary practice in the electro-plating factories to polish the articles before plating. This is done by means of a circular hair-brush, more or less hard,

as required, fixed upon a lath, and a thin paste made of oil and pumice-stone ground as fine as flour. By this process the surface of any article can be smoothened and polished; but a little experience is required to ensure success, and enable the operator to polish the surface equally without leaving brush marks. We need scarcely say, that after this process the article must be cleaned in potash before it is plated.

Second Method.—Instead of stripping off the silver by means of acid, it is a more common and preferable mode to brush off the silver by the operation just described. In this case the brushings must be collected, dried, and burned; this may be done in an iron pan, keeping it at a red heat until all carbonaceous matters are consumed; the remainder is collected and fused with carbonate of soda or potash, when the silver is obtained, in combination with a little copper. The copper may be afterwards separated by cupellation, or by fusing the alloy in a crucible, and adding, when in fusion, nitrate of potash, which oxidises the copper and leaves the silver pure. Or dissolve the alloy in nitric acid, then precipitate the silver with common salt as a chloride, and the copper is left in solution; collect the chloride on a filter, dry and fuse with carbonate of soda as described (page 138), and the silver will be got pure.

CYANIDE OF SILVER AND POTASSIUM: ITS DECOMPOSITION DURING THE PLATING PROCESS.—The silver salt in the plating solution is a true double salt, being, as already described, a compound of one equivalent of cyanide of silver and one of cyanide of potassium, two distinct salts. In the decomposition of the silver solution by the electric current the former, cyanide of silver, is alone affected: the silver is deposited, and the cyanogen passes to the positive plate or electrode. The cyanide of potassium is therefore set at liberty upon the surface of the article which is receiving the silver deposition, and its solution being specifically lighter than the general mass of the plating solution, rises to the top: this causes a current to take place along the face of the article being plated. If the article has a flat surface, suppose that of a waiter or tray, upon which a prominence exists, such as a mounting round the edge, say a gadroon pattern (see

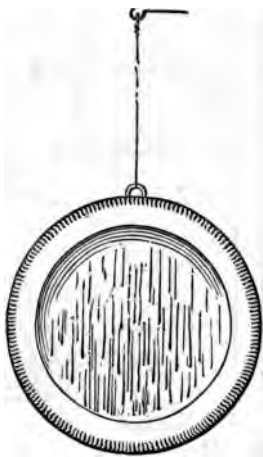


Fig. 43.

Fig. 43), it will cause lines and ridges from the bottom to the top, as already described at page 92. Newly-formed solutions are most subject to produce this annoyance.

OTHER EFFECTS PRODUCED IN WORKING.—As the cyanogen, which is transferred from the article, combines with the silver plate forming the positive electrode, the latter is dissolved by the free cyanide of potassium, which the solution must have to be in good working condition; and, being specifically heavier, it sinks to the bottom, by which a current is excited downwards. This is of no greater annoyance than that it renders the

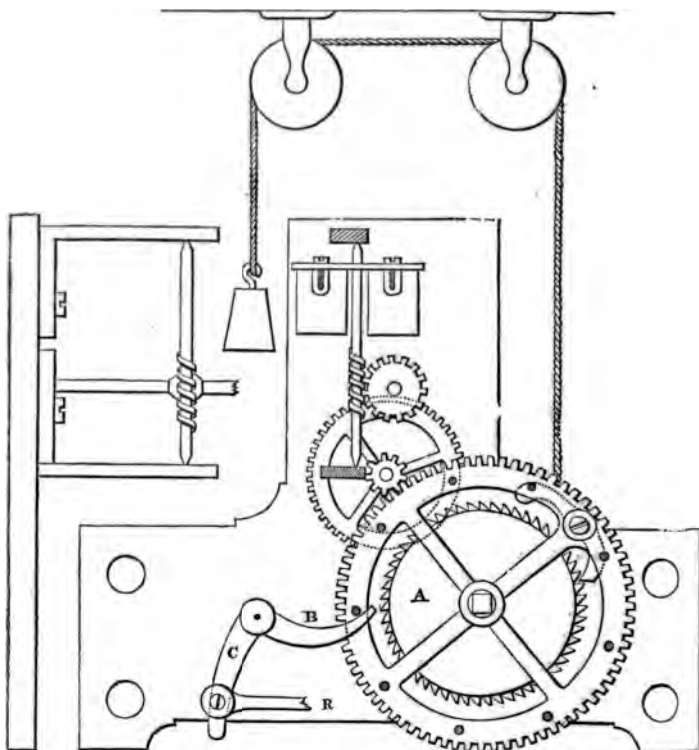


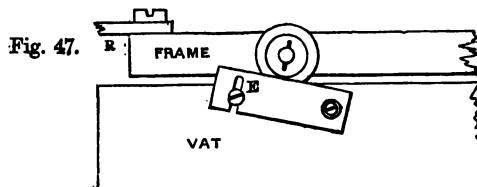
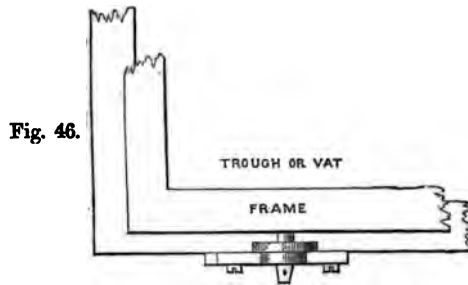
Fig. 44.

Fig. 45.

solution of unequal density, which in its turn yields an unequal deposit, more being deposited upon the lower parts of the article than on the upper. The silver plate or electrode is rapidly destroyed at the surface

of the solution; if a part of the silver be above it, the plate gets cut through as if done by a rough-edged knife. In a new solution, which contained $1\frac{1}{2}$ ounces of silver to the gallon, we have found, after six hours, just before taking out the articles, that the top part of the solution contained 200 grains of silver less, and the bottom part 200 grains more per gallon, than when the articles were put into it. These difficulties and annoyances may, however, be nearly surmounted by keeping the articles in motion: agitating or stirring the solution occasionally would also obviate these annoyances; but this is not advisable, for if the sediment (which always forms) were stirred up it would settle upon the face of the articles and make them rough. Where there is engine power it is an easy matter to keep the articles in motion; but where this power is not available, a very simple apparatus, invented by the late Mr. Alex. Mitchell, of Glasgow, may be fitted up at a trifling cost, to give the necessary motion by clockwork. The foregoing sketch exhibits this apparatus.

MACHINE FOR MOVING GOODS WHILE SUBJECTING TO THE ELECTRO-PLATING PROCESS.—Fig. 44, side elevation, with front frame off; Fig. 45,



end elevation of that part of front frame where the fly is held; Figs. 46 and 47, the plating vat, with frame moving on inclined plane.

The large wheel A, Fig. 45, is propelled by a weight suspended from

the roof by a cord, which winds round its barrel, the same as common clockwork. The circumference is studded with small pins, which catch the arm B, moving it in a downward direction, and consequently moving the arm C in a forward direction. The latter being attached to the frame by a small rod R, Figs. 45 and 47, moves it up the inclined plane E, Fig. 47, until the pin fixed in the wheel A passes the end of the arm B. The frame then moving down the incline E, brings B in gear with the next pin, and the same motion again takes place, and so on successively. The speed is regulated by the train moving in an endless screw fitted on the last wheel of the arbour of a fan. The four holes in Fig. 45 are for bolts or pillars for screwing the two frames together. The frame has four pulleys and inclines, the latter adjustable to a greater or less degree by the screw and groove at E.

Many large establishments have machines for moving the articles in the solution, as it not only prevents the evils above referred to, but facilitates the deposit; where there was no machine we have seen a boy employed for keeping the articles in motion.

DEPOSIT DISSOLVING OFF IN SOLUTION.—In depositing any metal, but more particularly such as require solutions having an excess of the solvent, like cyanide of potassium in the depositing of gold and silver, care should be taken that nothing stops the current of electricity suddenly, while the article being deposited upon remains in the solution, otherwise the metal deposited will speedily dissolve off. This we have often experienced, and many others have no doubt done the same. Indeed, we have seen a beautiful deposit going on, and have left the operation with great hope of excellent results, but on returning some time after have found the whole dissolved off. And often, when the process was apparently going on well, and the articles had been in the solution the usual time to receive a fair coating of metal, upon taking them out and weighing them, there was hardly any perceptible difference from the original weight; in short, there had been no material deposit. These phenomena will be found to occur when the solutions and the batteries are apparently in the best condition for working, and when the article upon which the deposit is going on, and the pole or plate of metal forming the positive electrode, are at a considerable distance from each other. But before explaining what we consider to be the cause of these annoyances, we will refer to another phenomenon connected with them, which is of great interest, so far as the principles we have been discussing are concerned, which is that only the solvent element in an electrolyte is transferred by the electric current.

OPPOSITE CURRENTS OF ELECTRICITY FROM VATS.—If, under the circumstances referred to, and when the deposit has gone on for some time, the wires connecting the battery with the electrodes in the depositing solution be disconnected, and a metallic connection be made between the articles that have received the deposit and the silver electrodes or plates, a current of electricity nearly as strong as that from the battery will pass through the connections, but in the opposite direction from that which was obtained by the battery. Indeed, if articles and silver poles were connected with another vat or decomposing cell, they would form a battery to this second vat, and produce a deposit at first nearly equal to the original battery; the current, however, would gradually weaken until it ceased. The cause of these actions and reactions is this: the article being plated with silver, or other metal, in connection with the battery, exhausts the solution of silver around it, leaving it in free cyanide of potassium, while around the sheet of silver which is serving as the positive electrode the solution is, on the contrary, becoming saturated with silver, so that we have all the conditions necessary to constitute a battery, having silver electrodes in two kinds of solution—the one capable of dissolving silver, the other not. The silvered articles become the positive metal in this battery, and the metal is speedily dissolved off, and thus the annoyances described above takes place. From these remarks the reader will perceive that even when the batteries are in connection, and the deposition going on from the moment the deposition of metal begins, there also arises an opposite current of electricity, tending to neutralise the effects of the battery, which current goes on increasing in quantity, neutralising the other. We have experienced great disappointment before knowing the cause. When an extra thickness was required upon the articles, and we allowed them to remain in the solution, in connection with the battery, for a longer time, we found when re-weighed that they had got less than when kept in for the ordinary time; indeed, it was a common experience that, towards the end of the operation, the batteries became very sluggish in their action. It is not merely the neutralising of the battery current, and the cessation of deposit, but the newly deposited silver being suspended in a solvent, it is liable to be dissolved off, so that in this case, as we have said, there may, at the termination of the ordinary period, be little or no silver deposited on the articles intended to be plated. Motion in the silver or depositing solution will prevent all these annoyances; and this being now generally adopted, these phenomena are not now observed, but the effects take place less or more in every solution.

TEST FOR THE QUANTITY OF FREE CYANIDE OF POTASSIUM IN SOLUTIONS.
 —It has been already mentioned that the cyanide of silver, as it forms upon the surface of the silver plate, is dissolved by the cyanide of potassium: this renders it necessary to have always in the solution free cyanide of potassium. Were we to use the pure crystalline salt of cyanide of potassium and silver, dissolved in water, without any free cyanide of potassium, we should not obtain a deposit beyond a momentary bluish, as the silver plate or electrode would get an instantaneous coating of cyanide of silver, and this not being dissolved, the current would stop. The quantity of free cyanide of potassium required in the solution varies according to the amount of silver that is present, and the rapidity of the deposition. If there be too little of it, the deposit will go on slowly; if there be too much, the silver plate will be dissolved in greater proportion than the quantity deposited, and the solution will consequently get stronger. The proportion we have found best is about half by weight of free cyanide of potassium to the quantity of silver in solution; thus, if the solution contains two ounces of silver to the gallon, it should have one ounce of free cyanide of potassium per gallon. This is known by taking some nitrate of silver, dissolving it in distilled water, and placing it in a common alkalimeter, graduated into 100 parts, Fig. 49. The proportion of the nitrate of silver in the solution is such that every two graduations of the solution should contain one grain.

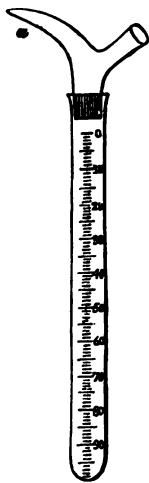


Fig. 49.

A given quantity of the plating solution is now taken—say one ounce by measure, and the test solution of nitrate of silver is added to it by degrees, so long as the precipitate formed is re-dissolved; when this ceases, the number of graduations is then noted, and the following equation gives the quantity of free cyanide. Every 175 nitrate of silver are equal to 130 cyanide of potassium in solution. Suppose 20 graduations were taken equal to 10 grains nitrate of silver, then $175 : 130 :: 10 : 7.4$ grains free cyanide of potassium. This, multiplied by 160, the number of fluid ounces per gallon, will make about $2\frac{1}{2}$ ounces. We have taken 2 graduations to one grain of nitrate of silver, that the solution may be considerably dilute and less

liable to error. The following table is calculated at a half grain nitrate of silver to the graduation, and will be a guide to the student or workman: the quantity of solution tested is one ounce by measure.

Number of graduations used.	Free cyanide per gallon.		
	oz.	dwt.	gr.
1	0	2	13
2	0	5	3
3	0	7	16
4	0	10	6
5	0	12	19
6	0	15	9
7	0	17	22
8	1	0	13
9	1	3	1
10	1	5	12
11	1	8	5
12	1	10	19
13	1	13	8
14	1	15	22
15	1	18	11
16	2	1	2
17	2	3	14
18	2	6	2
19	2	8	11
20	2	11	0

Another method may be adopted: if, for instance, we dissolve a small quantity of sulphate of copper, and add to it an excess of ammonia, there is produced a deep blue colour; cyanide of potassium will destroy the blue colour in a fixed chemical proportion: to obtain this proportion, take 10 grains of pure cyanide of potassium and dissolve in water; then take a certain quantity, say 100 grains, of sulphate of copper, and convert it into ammoniuret, the whole measuring a given quantity, and pour from an alkalimeter this blue liquor into the cyanide of potassium till it ceases to destroy the colour, then mark the number of graduations required, and that amount of copper solution will represent 10 grains cyanide of potassium; a quantitative test will thus be got for the full cyanide of potassium in the solution, and should be used as follows:—Say that the colour of 60 graduations of the blue solution was destroyed by the 10 grains of cyanide of potassium, then to test the quantity of free cyanide of potassium in the plating solution, take 60 graduations of the blue liquor in any convenient vessel, and add to it from an alkalimeter the plating solution till the colour of the blue liquor is destroyed, then note the quantity which contains 10 grains free cyanide, from which the quantity in the whole solution may be calculated.

ANALYSING THE SILVER SOLUTION.—In extracts from foreign journals, given in the *Chemical Society's Journal* for last year, 1874, appears the following, taken from *Dingl. Polyt.*:—

"First. The total quantity of potassium existing as potassium cyanide, silver potassium cyanide, carbonate and cyanate of potash, is first determined by mixing 20 CC of the bath solution with 14 CC of acetic acid, of the strength of 20 per cent., evaporating and extracting the residue with absolute alcohol, evaporating the alcohol, and heating the residue with hydrochloric acid, and weighing the salt as KCl (chloride of potassium).

"Second. The potassium in combination as cyanide of potassium and cyanide of silver is determined as chloride by precipitating the silver with ammonia sulphide from 20 CC of solution, and calculating the potassium chloride from the silver sulphide obtained.

"Third. The potassium existing as carbonate is determined by adding calcium chloride, and weighing the calcium carbonate precipitate.

"Fourth. Knowing that in the impure cyanide, if used in the manufacture, there is for every 7 equivalents of cyanide of potassium 3 equivalents of cyanate, the amount of cyanate in the bath may be calculated.

"Lastly. Deducting from the total quantity of potassium chloride obtained in (first) the quantity of the same salt equivalent to the silver potassium cyanide, the potassium carbonate and potassium cyanate, as determined in (second, third, and fourth) the remainder, is the potassium chloride equivalent to the cyanide of potassium which was present as such in the bath solution. The determination of this quantity of free cyanide of potassium is the whole object of the analysis, as upon it depends the capacity of the bath to take up fresh quantities of silver, and to be used for further electroplating operations."

This is certainly a very tedious, roundabout, and uncertain way of getting at the free cyanide of potassium, and can only be performed by an experienced chemist. If the electro-metallurgist wishes to ascertain the state of his solution, as to the different salts present, as near an approximation can be got by the following simple process. We have already given the method for taking the quantity of free cyanide of potassium:—To know the quantity of silver, take one ounce of solution and evaporate to dryness, and fuse the dry mass in a small crucible. The silver will be got as a small *pril* at bottom, and can be weighed; or, by adding to an ounce of the solution diluted hydrochloric acid in excess, which precipitates the silver as a chloride, collect the precipitate upon a weighed filter, wash it, and then dry at steam heat and weigh the whole, deduct the weight of the filter, and three-fourths of the weight of the precipitate is silver.

To one ounce of the solution diluted add nitrate of silver so long as a precipitate is given, then wash by filling up the vessel several times and pouring off the clear; then add to the precipitate nitric acid, diluted with half water, which dissolves all the silver not cyanide. This is decanted off, and a little muriatic acid added, and the silver obtained as a chloride to be filtered, washed, and dried as above. One-half of the weight of this precipitate approaches closely to the amount of cyanate of potash, or carbonate of potash, the difference in their equivalents not being great. By multiplying the results by 160, the quantity of each per gallon of solution is obtained. If there has been any chloride salt present in the solution, the chloride of silver formed will remain in the insoluble portion in the nitric acid. However, the electro-metallurgist seldom requires an analysis of his solutions, as the free cyanide of potassium, in relation to the silver present in the solution, is the principal matter requiring attention.

RATE OF DEPOSITING SILVER.—When articles are taken out of the solution they are swilled in cold water, and then put into boiling water: they are afterwards put into warm sawdust. Sawdust from boxwood is best, but that from mahogany or other wood, having no rosin in it, will do, which dries them perfectly. Their colour is chalk-white. They are generally weighed before being scratch-brushed; that is, brushed with the fine wire-brushes and stale beer, as already described. Although this operation does not displace any of the silver, still in taking off the chalky appearance, there is a slight loss of weight; the appearance after scratching is that of bright metallic silver. Any thickness of silver may be deposited by continuing the operation a proper length of time and keeping batteries in order. One ounce and a quarter to one ounce and a half of silver, to the square foot of surface, will give an excellent plate, about the thickness of thin writing paper.

BRIGHT DEPOSIT.—A little sulphide of carbon added to the plating solution prevents the chalky appearance, and gives the deposit the appearance of metallic silver; the reaction which takes place in this mixture is not yet understood. The best method of applying the sulphide of carbon is to put one or two ounces into a large bottle, then fill it with strong silver solution, having an excess of cyanide of potassium, and let it repose for several days, shaking it occasionally. A little of this silver solution is added, as required, to the plating solution, which will give to the articles plated the same bright appearance as if scratched. It is also found that the presence of sulphide of

carbon improves the working condition of the plating solution. We have already said that in the early history of the art, from want of practical knowledge, sometimes the metal deposited was rough and in little quantity, lead mounts not covered, and the deposit blistering, &c., in these circumstances the solution was blamed, and it was considered better to make a new solution than to waste time in trying to mend the old; a solution working twelve months was considered very satisfactory: the silver in old solutions was precipitated by muriatic acid and recovered by fusion. We have tried sulphuric and nitric acids to neutralise the alkalies, and washing the precipitated cyanide, and re-dissolving it in cyanide of potassium, but we seldom got satisfactory results. Such a practice as abandoning the old solution and making up new ones is now very seldom required. With careful management, paying attention to the quantity of silver deposited, and the quantity dissolved from the electrodes, and the addition now and then, when the action gets sluggish, of a little cyanide of potassium, and occasional stirring; a solution improves by working. We know of silver solutions that have been wrought daily upwards of ten years, and are still in excellent condition.

DIFFERENT METALS FOR PLATING.—Silver may be deposited upon any metal, but not upon all with equal adhesion. Copper, brass, and German silver are the best metals to use for plating upon; iron, zinc, tin, pewter, and Britannia metal are much less suited for plating; lead is not a good metal to plate—from its softness it easily yields to the pressure of the burnisher: nevertheless, all these metals and alloys may be and are plated, but cannot give the satisfaction which brass, copper, or German silver afford. In plating upon alloys having tin in them, such as Britannia metal, they must not be dipped into nitric acid previous to plating; but into a hot and strong solution of caustic potash or soda for five minutes, and put directly into the plating solution, which should have an excess of cyanide of potassium, and the battery should be as strong as the liquor will admit of without gas being evolved, until covered, when the silver may be thickened by an ordinary solution and battery.

Iron is not plated with silver direct with the battery. When plating iron, it is prepared as stated at page 119, and a bluish of copper is deposited upon it in the cyanide of copper solution, and it is removed directly from that to the silver bath, so that the silver is deposited upon the copper surface. Zinc may be plated in the same way, but that metal is never used alone as a basis for silver-plating.

ELECTRICITY GIVEN OFF FROM SANDY DEPOSITS.—We may mention here what we have often experienced, that when depositing silver upon a large surface, and the solution in relation to the battery being in the condition to give the sandy deposit, or rather when the deposit has gone on for a long time and the solution not been agitated, so that it has become very much exhausted of silver round the article, the deposit occurs as an impalpable powder like flour: sometimes the grains were a little coarser. The practice in such cases was to lift the articles from the solution and place them in boiling water, and after steeping there some time, to take them out and place them on the sawdust, when the heat of the metal soon caused them to dry. The powder adheres to the surface, which looks like as if thickly dusted over with flour. We have repeatedly observed when such a deposit was on a large surface, such as a tray or waiter, that when the hand was drawn suddenly over the surface the same effect was produced as when the hand is drawn over an electrified handkerchief or sheet of paper, accompanied with a crackling noise and pricking sensation; but never having chanced to be in the dark at the time, no light was visible from the surface rubbed. Although these are the conditions under which the observations were made, the phenomena were not produced every time these conditions were found. It is probably caused by the fact that this kind of deposit, which is of a chalky appearance, is a bad conductor of electricity; and as the boiling water was often very impure, holding salts in solution, the rapid evaporation of the water from the surface of this sort of deposit might leave it excited for a short time, and the hand being drawn across at the time of excitation electricity was liberated. When this powder is placed under a microscope it is seen to be composed of an aggregation of crystals of metallic silver of a matted appearance and great beauty. When the solution and batteries get into the conditions stated, and the articles being small, these crystals grow upon one another. We have got, for example, upon the point of a fork, a tuft of these crystals, fully an inch in diameter, growing out like mould upon flour, forming a sort of fungus upon the point of the fork; but when taken out of the solution the fibres collapsed, and had a spongy appearance. Dr. De la Rue, who examined some of this deposit magnified 200 times its natural size, says, "It is a most splendid arborescent assemblage of crystals, and presents us with an extreme case of crystallisation in electro-metallic deposits;" we give a figure of the appearance, as seen by us, also magnified about 200 times (see Fig. 49). When this kind of crystallisation begins they are formed rapidly. We have had similar formations in depositing tin from chloride.

We have, however, obtained groups of crystals in mass of the same appearance, where the crystals were large and visible, each group weighing several pennyweights; but deposited metals are all less or more crystalline, according to circumstances. Motion of the articles,

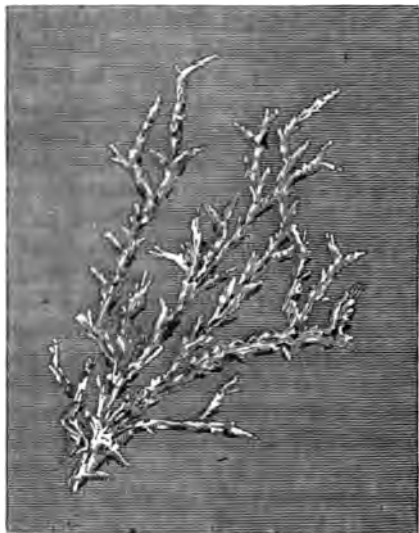


Fig. 49.

when battery and solution are in proper order, prevents the crystalline deposit. Upon the crystalline structure of deposited metals, see an article by Dr. Warren de la Rue in *L. and E. Phil. Mag.*, 1846.

THE OLD METHOD OF PLATING.—Many objections were urged by interested and other parties against the application of electro-deposition to the purposes of plating, as a branch of manufacture, either as a competitor or substitute for the old method, technically called *Sheffield plate*—so called because Sheffield was a principal seat of that manufacture. To enable our readers to form a proper estimate of the objections urged, by enabling them to judge of the relative importance and value of the two processes, we shall add a brief description of the old method.

An ingot of copper being cast, was filed square and smooth, and a piece of silver was placed upon it, the two surfaces being perfectly clean: a little powdered borax having been introduced between the two metals,

they were bound together with iron wire, and then heated in a furnace nearly to the melting point; the small quantity of borax increased the fusibility of the two metals at their surface, and thus they were fused together. When fusion was effected the metals were subjected to the dilating process of heavy rollers, the dimensions in length and width being regulated according to the articles to be made. This sheet formed the base or foundation of every article, of whatever shape or form, and however it was to be ornamented when finished.

To produce ornaments, leaf silver was stamped in iron dies representing the ornaments required, which, when removed from the dies, were filled with an alloy of lead and tin. These were then soldered upon the flat or shaped plain surface with soft solder, which melts at a very low temperature: thus were produced the silver edges or mounts.

The quality of the ornament depended entirely upon the price of the article; but whatever the quality, all ornaments in the old mode of plating were so made, the only difference being the thickness of the silver leaf used. Ornamental feet, handles, knobs, &c., were made in the same manner, being struck up in *two* parts, filled with lead and tin, soldered together with soft solder, and afterwards soldered to the main body. Articles (such as table candlesticks) which would be too heavy if filled with lead, were filled with rosin, pitch, or any other similar substance, for the purpose of preventing the article being flattened by pressure. Hence it is evident that no *solid* article could be made by the old mode of plating, the only way of producing articles being to work them up by the hammer, or to strike them in dies from a flat surface; and being restricted to the use of soft solder, on account of the plated metal and the shells of silver, forming the edges, not supporting the required heat to melt *silver* solder, it is equally evident that the joinings so constructed would be easily removed either by force or heat.

The nearest approach to *solid* articles made by the old method of plating were forks and spoons: these were generally made of iron, thin silver being soldered upon the surface, which was afterwards dressed smooth and polished.

The heat used in this operation was merely that of an ordinary soldering iron; because, were a greater heat applied, the silver would form an alloy with the tin and lead of the solder and melt: the same heat that cemented the metals in the first instance would be sufficient to disunite them; and thus when these forks were exposed in hot gravy, the solder was liable to become soft, and the silver covering, yielding readily to the knife, to peel up or become abraded, in consequence of the soft intervening metal.

ADVANTAGES OF ELECTRO-PLATING.—The advantages offered to the plater by the electro-process are many, arising from the fact of the articles being plated *after*, instead of *before* being manufactured. This at once entirely removed all those restrictions on taste and design under which the plater was forced, by the nature of his process, to labour.

The following may be considered some of the principal differences between the two processes of plating,—the old method and the electro-process :—

1. The electro-plater is not limited in the use of the metal upon which he plates. There is generally used, as the bases of all electro-plated goods, a hard white metal, which possesses the ring and approaches very nearly to the colour of silver.

2. The electro-plater is not restricted to the use of soft solder, which melts at a very low temperature, and forms a very insufficient joint, besides preventing any sound or ring in the article so soldered. Where cheap goods are required, soft solder may be used in *this* process as well as in the old, they are always open to the same objection. All goods of superior quality made for the electro-process, are soldered with what is termed in the trade *hard silver solder*, composed of two parts of silver and one part of brass melted together, which is not affected by any ordinary degree of heat, and presents a joint as strong as the metal itself.

The common solder of braziers may also be used with advantage: it is very hard and durable, and requires a strong heat to melt it.

3. The electro-plater in producing ornamental articles is not obliged to incur the expense of cutting iron dies for every minute portion; being under no restriction, he models his pattern, and by casting and chasing in *solid* metal, produces an exact copy, which is *afterwards* plated or gilt.

Thus any pattern which can be executed in silver may be readily made in plate by this method.

4. The junction of the plating with the metal below by the electro-process is perfect, without the presence of any intervening substance: the forks and spoons thus made are not open to the objection of the old process, and are found to answer all the purposes of silver in sound, appearance, and wear: they are generally tested, previously to polishing, by exposure in a furnace to a red heat.

5. From the facility with which *old* goods may be now restored, these goods bear an intrinsic value; whereas before the introduction of the electro-process, a plated article worn through in any part was valueless. However, it is proper to state that electro-plated goods are not necessarily first class; inferior manufactured articles may be, and are electro-

plated, as well as the best, and the amount of silver deposited may be very thin. There are a large quantity of goods made of Britannia metal, and coated with only a few pennyweights of silver per square foot, which in appearance are equal to the best plated articles, but are really not suited for general use. We have seen a whole tea set, silver plated, sold for 30s., which in appearance vied with sets five times the price, and when used only two or three times in the year, would last with ordinary care a lifetime, and be the pride of the good housewife not only to keep in order, but to have everything in keeping, and so raise the taste of the whole family. We have never seen a silvered tea set produced in a working-man's house, but we have found everything else about the family indicative of taste and comfort.

OBJECTIONS TO ELECTRO-PLATING.—Several objections to the electro-process were long and keenly urged, but which may all be reduced to the following:—

1. Deposited metal is crystalline, and therefore, though it may give in appearance a silver coating, it must necessarily be full of minute interstices between the crystals: hence when a metal, such as copper, is plated, it is liable to be acted upon by the atmosphere, or injured by whatever is brought into contact with it.

This objection was not without foundation, as all deposited metals are crystalline in texture, but they do not necessarily leave interstices: the objection, however, is almost entirely removed by keeping the articles in motion during the deposition: by motion and proper arrangement of battery we have deposited silver of as high specific gravity as hammered silver, which could not be the case if it were porous.

2. As only pure silver is deposited, it must necessarily be soft, and consequently liable to abrasion and more rapid wear.

This objection is also partly true. Only pure silver can be deposited; but it is not necessarily soft: the quality of the deposit in this respect depends (as already noticed) a great deal upon the nature of the solution and the battery power. Intensity of battery gives hardness to the metal deposited. There is no complaint more common amongst the burnishers of electro-plated articles, than that the metal is hard; and it is far from being an uncommon occurrence, that some goods have to be heated so that they may be more easily burnished or polished. How far this annealing may affect the wear of the goods is not yet ascertained. That the silver is pure we think an advantage, hence the superior colour which electro-plated goods possess: besides which, purchasers are not subject to the risk of having plate much alloyed. How-

ever the goods are more easily tarnished by exposure, and require greater care and labour in keeping them clean.

3. The mounts or prominences of articles, which must have the greatest wear, have the least and thinnest deposit.

This objection is entirely without foundation, as the prominences have always the greatest portion of deposit, and the hollow parts the least.

A SUCCESSFUL OBJECTION.—At the commencement of the art, different manufacturers looked about to see how far it might be suitable for certain processes, such as for coating boilers for working stearine, &c.; and among other applications was the coating with silver the inside of copper saucepans instead of tinning. We remember in a large plating establishment that suitable apparatus were fitted up, and several sets of saucepans were plated, giving them what was considered a good thick plating; and when finished they looked like something that would take the market, and the most sanguine hopes were entertained of a large trade. Several pans were bought and reported upon favourably. At length a whole set was purchased for a certain club in the city, and after a few weeks the head officer of the kitchen, or some such official, called at the warehouse and, after introducing himself, spoke highly of the new saucepans, and promised to give them a fair chance, for which he received thanks *and nothing more*.

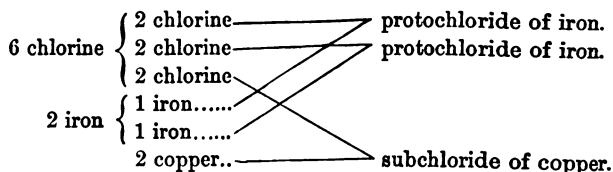
About a month after, the firm were startled by a letter in the *Times*, signed Robert Warrington, Chemist to the Apothecaries' Hall Company, warning the public against the use of copper saucepans silvered by the electro-process, he having had sent him for examination some pickles made in a pan so plated, that contained a large quantity of copper in solution. Application was at once made to Mr. Warrington to find whence the pickles had been obtained, and it was found that they had been sent from the club referred to. Investigation led to the discovery that the pan in which the pickles were made had been scoured by something that cut through the silver coating, exposing the copper; and that the pickles had been allowed to stand in this pan for several days, and then sent for testing. Five saucepans of the same size as the one complained of were coated respectively with 5 pennyweights, 10 pennyweights, 15 pennyweights, 20 pennyweights, and 25 pennyweights of silver: the one complained of had 20 pennyweights. These were sent to Mr. Warrington to test in any way he might consider proper for the safety of the public using them. The answer was that the 5 and 10 pennyweights coatings did not stand all the tests he had put them to; but the others had stood every test which he considered they would likely be put to in

use, and also to tests more trying than they would likely be subjected to. This report was published in the *Times* and other newspapers of the day, but without effect. There were no more sold, and they had to dissolve the silver off those plated, and have them tinned; and the opinion was that had this testing by Mr. Warrington preceded any sale, and had two sovereigns been given to the club official when he called and reported in their favour, it might have saved to the electro-metalurgist a large trade.

SOLID SILVER ARTICLES MADE BY THE BATTERY.—Silver may be deposited from its cyanide solution upon wax moulds polished with black-lead, almost as easily as copper; but for this purpose it is better to have the solution much stronger in silver than for plating. We have found that 8 ounces of silver to the gallon of solution make a very good strength. Nevertheless, no articles are made in silver by depositing upon wax in this manner. Strong solutions of cyanide of potassium and silver act upon wax, and would soon destroy a mould. The method of making articles in solid silver by the electro-process has been already explained (page 69), namely, a copper mould is made by the electrotpe, and the silver is deposited within this mould to the proper thickness; after which it is kept in a hot solution of crocus mineral and muriatic acid, or boiled in dilute hydrochloric acid, which dissolves the copper without injuring the silver.

The method which we esteem as best for dissolving off the copper is this:—An iron solution is first made by dissolving a quantity of copperas in water, heat this till it begins to boil: a little nitric acid is then added—nitrates of potash or soda will do just as well; the iron, which is thus peroxidised, may be precipitated either by ammonia or carbonate of soda; the precipitate being washed, muriatic acid is added till the oxide of iron is dissolved. This forms the solution for dissolving the copper. When the solution becomes almost colourless, and has ceased to act on the copper, the article is removed, and the addition of a little ammonia will precipitate the iron along with a portion of the copper; but after a short time's exposure the copper is redissolved; the remaining precipitate is washed by decantation; a little ammonia should be put into the two first waters used for washing. When washed, and the copper dissolved out, the precipitate is redissolved in hydrochloric acid, and the silver article returned until the copper is all dissolved off. It is convenient to have two solutions of perchloride of iron, so that while the iron in the one is being precipitated, the article is put into the other. The persalt of iron will be found to dissolve the

copper more rapidly than muriatic acid alone: persulphate of iron must not be used, as it dissolves the silver along with the copper. The silver article is now cleaned in the usual way (page 139), and heated to redness over a clear charcoal fire, which gives it the appearance of dead silver, in which state it may be kept, or, if desired, it may be scratched and burnished. It will be observed that when ammonia is added to the solution of copper and iron, both these metals are precipitated together as a brown precipitate. After a little exposure, the copper redissolves, and the iron is at the same time peroxidised, having been previously reduced to the protoxide by the copper dissolving. As will be manifest by the following diagram, perchloride of iron is composed of 6 equivalents of chlorine, equal to 213, and 2 of iron, equal to 112. Copper is 64.



From this the reader will observe that 325 parts of perchloride of iron dissolve 128 parts of copper. When the persulphate of iron is used for dissolving copper, and ammonia is then added to the solution, the same results take place—the precipitation of both copper and iron. But the copper dissolves more quickly in the ammonia. However, with free ammonia, either with the chloride or sulphate, the oxidation of the metals is slower than with water alone. If it be desirable to recover the copper that has been dissolved, retain the ammoniacal solutions of copper, and neutralise by sulphuric or muriatic acids; then add metallic iron or zinc, and the copper is precipitated upon the iron or zinc in a metallic state, which may be collected and washed, and by fusion in a crucible along with a little borax, the metal is obtained pure.

Copper moulds intended for receiving a deposit must be protected on the back by some substance that will not take on the deposit or be affected by the solution. The substance generally used for this purpose is copal varnish; pitch has been used, and serves the purpose well in ordinary solutions; but when the solutions are very strong, as is used for solid deposit, it is liable to be acted upon, and renders the solution very muddy; besides, it is very brittle, and if great care is not taken it is liable to crack and admit the solution.

In the manufacture of solid silver articles, the electro-process has not yet been of extensive application: and in making duplicates of rare

objects of art and costly chased or engraved articles in silver, one prevailing objection remains, namely, they have no "ring," and seem, when laid suddenly upon a table, to be cracked or unsound, or like so much lead; this disadvantage is no doubt partly due to the crystalline character of the deposit, and partly to the pure character of the silver, in which state it has not a sound like standard or alloyed silver. That this latter cause is the principal one, appears from the fact that a piece of silver thus deposited is not much improved in sound by being heated and hammered, which would destroy all crystallisation.

We may mention that the same objections are applicable to articles made in gold by the electro-deposit; nevertheless, for figures and ornaments, and copies of antique objects, such objections are of no consequence. We have seen antique objects copied in silver by the electro-process, where the above defect was never noticed, and it is only for such articles that the solid deposit is at all likely to be used. For figures and richly chased objects, the above objections are not applicable.

DEAD SILVERING FOR MEDALS.—The perfect smoothness which a medal generally possesses on the surface renders it very difficult to obtain a coating of dead silver upon it, having the beautiful silky lustre which characterises that kind of work, except by giving it a very thick coating of silver, which takes away the sharpness of the impression. This dead appearance can be easily obtained by putting the medal, previous to silvering, in a solution of copper, and depositing upon it, by means of a weak current, a mere blush of copper, which gives the face of the medal that beautiful crystalline richness that deposited copper is known to give. The medal is then washed from the copper solution, and immediately put into the silver solution. A very slight coating of silver will suffice to give the dead frosty lustre so much admired. When large objects are required of a dead silver finish, it is obtained by having the solution in good working condition, and watching the deposit to take the article out of the solution at the proper time, before it gets the chalky appearance; and even when this has taken place, by allowing the article to remain a few minutes in the solution, without being in contact with the battery, this chalkiness will disappear. Care has to be taken that it is washed out the solution in *pure* water; if not, the surface will be stained, neither should it be touched with the fingers.

OXIDISING SILVER.—A very beautiful effect is produced upon the

surface of silver articles, technically termed oxidising, which gives the surface an appearance of polished steel. This can be easily effected by taking a little chloride of platinum, prepared as described at page 146, heating the solution and applying it to the silver when an oxidised surface is required, and allowing the solution to dry upon the silver. The darkness of the colour produced varies according to the strength of the platinum solution, from a light steel grey to nearly black. The effects of this process, when done along with what is termed dead work, is very pretty, and may be easily applied to medals, giving scope for the exercise of taste. Upon this we quote the following:—

“The high appreciation in which ornaments in oxidised silver are now held render a notice of the process followed interesting. There are two distinct shades in use, one produced by chloride, which has a brownish tint, and the other by sulphur, which has a bluish-black tint. To produce the former, it is only necessary to wash the article with a solution of salammoniac; a much more beautiful tint may, however, be obtained by employing a solution composed of equal parts of sulphate of copper and salammoniac in vinegar. The fine black tint may be produced by a slightly warm solution of sulphide of potassium or sodium.”—*Chem. Techn. Mittheilungen, von Dr. Ellsner.*

PROTECTION OF SILVER SURFACE.—All silver or plated articles are subject to tarnish by exposure to the air, especially in this country, where coals containing so much sulphur are used—the tarnish being generally a sulphide of silver. Deposited silver is more easily tarnished than standard silver.

Medals or figures silvered for the sake of their appearance ought to be protected from the air, or they very soon lose their silver colour; a medal may be put into a frame air-tight, and a figure should be covered with a glass shade: if the silver has been left dead, any attempt to clean it destroys its appearance. Varnishes have been tried to protect the silver from the atmosphere; but all varnishes, however colourless, detract from the silver lustre, and are not good. For ordinary purposes, medals may be very conveniently protected by laying a piece of common glass over the surface, cut to the exact size, and held close by a piece of paper pasted round the edges of both, and then a stout piece on the back. We have had silver medals preserved by this means for more than twenty years. Little round medals may be conveniently covered by watch-glasses, fastened on in the same manner.

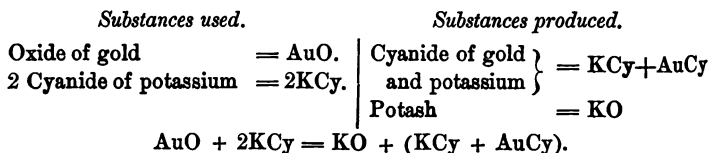
CLEANING OF SILVER.—A weak solution of cyanide of potassium, used as a wash over tarnished silver, will brighten it. This solution is sold in small bottles for this purpose, but it is not good, as it dissolves the silver rapidly, and is such a deadly poison that it must be used with great caution on articles that may be required for domestic purposes.

A variety of cleaning pastes and powders are used for silver or plated goods. Those containing mercury and oxide of lead should be avoided, for although they give a beautiful dark colour when newly put on, it soon blackens. The best paste we have found is a mixture of fine precipitated chalk, carbonate of magnesia, and oxide of iron. These materials are made into a paste, and rubbed upon the plate with soft leather: for wrought or chased surfaces a hard brush is best. The goods should be finished by polishing with leather and a little of this mixture in a dry state, which will give that fine dark mirror-looking colour so much admired. Common coarse whiting and flannel cloths should not be used, as they wear the silver rapidly.

ELECTRO-GILDING.

THE operation of gilding, or covering other metals with a coating of gold, is performed in the same manner as the operation of plating, with the exception of a few practical modifications, which we shall now notice in detail:—

PREPARATION OF SOLUTION OF GOLD.—The gold solution for gilding is prepared by dissolving gold in three parts of muriatic acid and one of nitric acid, which forms the chloride of gold. This is digested with calcined magnesia, and the gold is precipitated as an oxide; the oxide is boiled in strong nitric acid, which dissolves any magnesia in union with it. The oxide being well washed, is dissolved in cyanide of potassium, which gives cyanide of gold and cyanide of potassium and potash, thus—



By this method a proportion of potash is formed in the solution as an impurity; it is not, however, detrimental to the process. In preparing the oxide of gold there is always a little of the gold lost, to recover which the washings should be kept, evaporated to dryness, and fused.

Another and very simple method is this:—Make chloride of gold as described, and evaporate the solution to nearly dryness, which will drive off excess of acid there. Add a solution of cyanide of potassium to the chloride of gold, until all the precipitate first formed is redissolved; this gives chloride of potassium in the solution, which is not good. In the preparation of the solution by this means there are some interesting re-actions. As the chloride of gold has three equivalents of chlorine, the addition of cyanide of potassium causes violent effervescence, and no precipitate of gold takes place until all the chlorine is neutralised, which causes a considerable loss of the cyanide of potassium. There is always formed in this operation a quantity of

ammonia and carbonic acid, from the decomposition of the cyanate of potash; and if the chloride of gold be recently prepared and hot, there is often formed some aurate of ammonia (fulminate of gold), which precipitates with the cyanide of gold. Were this precipitate collected and dried, it would explode when slightly heated. On previously diluting the chloride of gold, or using it cold, this compound is not formed.

After the chlorine is neutralised by the potash, further addition of the cyanide of potassium precipitates the gold as cyanide of gold, having a light yellow colour; but as this is slightly soluble in ammonia and some of the alkaline salts, it is not advisable to wash the precipitate, lest there be a loss of gold: cyanide of potassium is generally added until the precipitate is redissolved; consequently all the impurities formed in these re-actions, namely, nitrate and carbonate of potash, with chloride of potassium and ammonia, are present in the solution. Notwithstanding, this solution works very well for a short time, and it is very good for operations on a small scale.

BATTERY PROCESS OF PREPARING GOLD SOLUTION.—The best method of preparing the gold solution is that described for silver (p. 135). Say the operator wishes to prepare a gallon of gold solution, he dissolves four ounces of cyanide of potassium in one gallon of water, and heats the solution to 150° Fah.; he now takes a small porous cell, and fills it with this cyanide solution, and places it inside the gallon of solution. The two solutions should be on a level. Into this cell is put a small plate of iron or copper, and attached by a wire to the zinc of a battery. A piece of gold is placed into the large solution, facing the plate in the porous cell, and attached to the copper of the battery; the whole is allowed to remain in action until the gold, which is to be taken out from time to time and weighed, has lost the quantity required in solution. By this means a solution of any strength can be made, according to the time allowed. The solution in the porous cell, except the action has continued a long time, will have no gold, and may be thrown away. Half an hour will suffice for a small quantity of solution; of course, any quantity of solution may be made up by the same means. A solution made in this way is free from all impurities except that existing in the cyanide of potassium. For all the operations of gilding by the cyanide solution, it must be heated to at least 130° Fah. The articles to be gilt are cleaned from oil or grease in the way described for silver, and dried, and then weighed: when gilt, they are weighed again: thus the quantity of gold deposited is ascertained. Any convenient means may be adopted for heating the solution. Where glass or stone-

ware vessels are used for holding the gilding solution, these are placed in another vessel, made of tinplate or iron, of the same depth, and filled to within an inch of the mouth with water, and placed upon a hot plate over a fire, or over gas burners, and the water heated to the boiling point. Some electro-metallurgists use enamelled iron pots for holding the gilding solution, which are heated directly, either with fire or gas. Such baths must have a wooden frame over the mouth, to prevent metallic contact with the rods suspending the articles being gilt. Great care has to be taken to get a proper enamel upon the pots, as many enamels yield to the solution; and when portions of the iron get bare in this way, the gold becomes reduced upon the iron, causing loss and annoyance. We prefer vessels of stoneware for the solution, and such vessels can be had, of ample size, for almost all articles requiring to be gilt. The heat of the solution is of considerable importance, both as to colour of the gold deposited and battery power. The hotter the solution the less battery power is required. Generally three or four pairs of plates are used for gilding, and the solution is kept at 130° to 150° Fah.; but one pair will answer if the solution is heated to 200° .

PROCESS OF GILDING.—The process of gilding is generally performed upon silver articles. The method of proceeding is as follows:—When the articles are cleaned, as described in our chapter on plating, they are weighed and well scratched with a wire brush, which cleanses away any tarnish from the surface, and prevents the formation of air-bubbles; they are then kept in clean water until it is convenient to immerse them in the gold solution. One immersion is then given, which merely imparts a blush of gold; they are taken out and again brushed, and put back into the solution, and kept there for three or four minutes, which will be sufficient if the solution and battery are in good condition; but the length of time necessarily depends on these two conditions, which must be studied and regulated by the operator.

Iron, tin, and lead are very difficult to gild direct; they therefore generally have a thin coating of copper deposited upon them by the cyanide of copper solution, and immediately put from this into the gilding solution.

CONDITIONS REQUIRED IN GILDING.—The gilding solution generally contains from one-half to an ounce of gold in the gallon; but for covering small articles, such as medals, for tinging daguerreotypes, gilding rings, thimbles, &c., a weaker solution will do. The solution should be sufficient in quantity to entirely cover the articles at once, so

that it should not have to be done bit by bit; for when there is a part in the solution and a part out, there will generally be a line mark at the point touching the surface of the solution. The rapidity with which metals are acted upon at the surface line of the solution is remarkable. If the positive electrode is not wholly immersed in the solution, it will in a short time be cut through at the surface of the water, as if cut by a knife. This is also the case in silver, copper, and other cyanide solutions, as before referred to.

MAINTAINING THE GOLD SOLUTION.—As the gold solution evaporates by being kept hot, distilled water must from time to time be added: this water should always be added when the operation of gilding is over for the time, not when it is about to be commenced, or the solution will not give so satisfactory a result. Where the gilding operation is continued successively for days, the water is added at night. The average cost of depositing gold is about 2d. per pennyweight.

The means for testing the free cyanide of potassium present by nitrate of silver, as described for silver, is not applicable to the gold solution; but it may be tested by the ammoniuret of copper (see page 151). To obtain a deposit of a good colour, much depends upon the heat and state of the solution and battery; it is therefore necessary that strict attention be paid to these, and also to the weight of gold deposited, and the loss sustained by the positive electrode. This should be ascertained daily, as the gold solution is very liable to change if the relative surface of the article receiving the deposit is not according to that of the positive plate.

The result of a series of experiments and observations continued daily throughout a period of nine months, shewed that in five instances only the deposit was exactly equal to the quantity dissolved from the positive plate. In many cases the difference did not exceed 3 per cent., though occasionally it rose to 50 per cent. The average difference, however, was 25 per cent. In some cases, double the quantity dissolved was deposited, in others the reverse occurred—both resulting from alterations made in the respective conditions; for in these experiments we varied, as far as practicable, the state of the solution and the relative sizes of the negative and positive electrodes.

The most simple method of keeping a constant register of the state of the solution is to weigh the gold electrode before putting it into the solution, and when taking it out, and compare the loss with the amount deposited; a little allowance, however, must be made for small portions of metal dissolved in the solution, from the articles that are gilt, which,

when gilding is performed daily, is considerable in a year. A constant control can thus be exercised over the solution, to which there will have to be added, from time to time, a little cyanide of potassium, a simple test of requirement being that the gold pole should always come out clean: if it has a film or crust upon it, that is a certain indication that the solution is deficient of cyanide of potassium. Care must be taken to distinguish this crust, which is occasionally dark green or black, from a black appearance which the gold pole will take, when it is very small in comparison to the article being gilt, and which is caused by the tendency to evolve gas. In this case an addition of cyanide of potassium would increase the evil; the black appearance, from the tendency to the escape of gas, has a slimy feel and appearance. This generally takes place when the solution is nearly exhausted of gold, of which fact this appearance, taken conjointly with the relative sizes of the electrodes, is a sure guide.

Before these facts were patent to us, gold solutions were always going out of order, so that every few months a new solution had to be made: the old one being evaporated to dryness, and the residue fused in a crucible, and the gold recovered as a button at bottom of crucible; but by experience and attention to the conditions stated above, the quality of the solution was kept in a condition suitable to the requirements of the work. Solutions are now kept in good condition for any length of time. We know solutions in daily use for upwards of ten years and still good.

TO REGULATE THE COLOUR OF THE GILDING.—The gold upon the gilt article, on coming out of the solution, should be of a dark yellow colour, approaching to brown; this, when scratched, will yield a beautifully rich deep gold. If the colour is blackish it ought not to be finished, for it will never either brush or burnish a good colour. If the battery is too strong, and gas is given off from the article, the colour will be black; if the solution is too cold, or the battery rather weak, the gold will be light coloured; so that every variety of shade may be imparted. A very rich dead gilt may be made by adding ammoniuret of gold to the solution just as the articles are being put in.

If a bright clear yellow gilding is wanted that will require no scratch brushing, add to the solution a small quantity of caustic soda. This is well suited for gilding filigree work, or tender articles that will not stand brushing; indeed, filigree will never produce a satisfactory colour if it requires brushing; for gilding ordinary work, keep the gold solution *strong*, and the colour of the gilding when it comes out the solution will

be a rich orange, and scratch-brushing will give that deep rich gold colour so much admired in gold plate.

COLOURING OF GILDING.—A defective coloured gilding by the battery may, however, be improved by the same method as that adopted in the old process to colour gilding or gold, namely, by the help of the following mixture:—

3 parts Nitrate of Potash.

1½ Alum.

1½ Sulphate of Zinc.

1½ Common Salt.

These ingredients are put into a small quantity of water, to form a sort of paste, which is put upon the articles to be coloured; they are then placed upon an iron plate over a clear fire, so that they will attain nearly to a black heat, when they are suddenly plunged into cold water: this gives them a beautiful high colour. Different hues may be had by a variation in the mixture.

TO DISSOLVE GOLD FROM OLD GILT ARTICLES.—Before regilding articles which are partly covered with gold, or when the gilding is imperfect, and the articles require regilding, the gold should be removed from them by putting them into pure strong nitric acid; and when the articles have been placed in the acid, by adding some common salt, not in solution, but in crystals. By this method gold may be dissolved from any metal, even from iron, without injuring it in the least. After coming out of the acid, the articles must be polished. The best method, however, where it can be adopted, is to brush off the gold as described for silver (page 145), which gives the polish at the same time.

TO RECOVER THE GOLD.—When the gold is dissolved off by the acid, and when it ceases to dissolve the gold rapidly, the acid should be diluted with several times its bulk of water, and then soda or potash added, till the greater portion of the acid is neutralised. Potash is best to use, for by a short time's evaporation and allowing the solution to cool, the greater portion of the potash is crystallised, and may be collected to use for dissolving silver from copper (page 144). The mother liquor containing the gold is now to be diluted with a large quantity of water. A solution of sulphate of iron (copperas) is then added to this so long as a precipitate is formed; when this settles down, it is carefully collected upon a paper filter, washed and dried, and then fused in a crucible with a little borax and common salt, and the gold is found as a button at the bottom of the crucible.

When gold is brushed off, the brushings are burned at a red heat, and the residue fused with carbonate of soda and a little borax; in this case the gold will not be pure, and will have to be refined, which is done by putting the gold into a crucible of some size, and bringing it into a state of fusion, and adding to the crucible from time to time small portions of nitrate of potash; that crystallised from the liquor will do, which oxidises all the inferior metals. When the fused metal is seen bright, without any apparent waviness passing over its surface, the crucible is removed from the fire, and the metal poured out; but as this may cause a loss where the quantity is small, it is better to allow the crucible to cool, and break it, when the refined gold is got as a little ball. If silver is present, which will be if the gilding has been brushed off silver, this has to be separated from the gold by an after operation called parting. The gold has to be fused again along with two or three times its weight of silver, and the alloy hammered into a thin plate, and digested in pure nitric acid, which dissolves out the silver, and leaves the gold as a skeleton, which is washed, and may be remelted, or used as it is. The silver is now recovered by precipitating it with common salt, as described at page 144.

OBJECTIONS TO ELECTRO-GILDING.—Objections have been made to the application of electro-gilding to the arts, of the same kind as those urged against electro-plating; but the now almost universal adoption of this process by gilders, because of the perfection to which the art is brought, forms the best answer we can give to such objections. However, let us take a hasty glance at the old process and its consequences, that we may be enabled to judge of the comparative merits of both methods.

Before the introduction of electro-deposition there were several methods of gilding practised by the trade, the principal of which was by making a thin amalgam of mercury and gold, and giving the surface of the metal to be gilt a thin wash with this, and then submitting them to a strong heat; the mercury being gradually dissipated, the gold remained fixed upon the articles. This process was most pernicious, and destructive to human life; the mercury, volatilised by the heat, insinuates itself into the bodies of the workmen, notwithstanding the greatest care; and those who were so fortunate as to escape for a time absolute disease, were constantly liable to salivation from its effects. Paralysis was common among them, and the average of their lives was very short; it was estimated as not exceeding thirty-five years. It is difficult to believe that men could be found to engage

in such a business, reckless of the consequences so fearfully exhibited before them; and it would naturally be thought they would hail with pleasure the introduction of any process which would put a stop to such a dreadful sacrifice of human life. But it is very difficult to overcome interest and prejudice, even when the object to be gained is of such vast importance.

Previous to the electro-process, the Messrs. Elkington and others, to avoid the use of mercury as much as possible, had introduced processes of gilding without mercury, by dipping the articles into certain solutions of gold, by which the surface obtained a film of gold; but these processes did not suit all kinds of work, nor fulfil all the requirements of gilding. We believe that trinkets and jewellery are still gilt by a mere dip into a solution of gold, and then washed; but on such there is scarcely an appreciable quantity of gold, still there is sufficient to give to the surface the colour of the precious metal.

EFFECTS OF CYANOGEN ON HEALTH.—The effects produced upon the health of those who work constantly over cyanide solutions are not yet fully tested, in so far as it shortens life, by which we could form a comparison with the old process; for every new trade or operation gives rise to a new disease, or some new forms of an old disease. Having ourselves inhaled much of the fumes of that “ominous” gas given off from the cyanide of potassium solution, we are not prepared to stand its advocate, but would rather warn all employed at the business, or who may in any degree have to do with these solutions, to be very careful not to use too much freedom. The hands of those engaged in gilding or plating, should the skin be broken, are subjected to ulceration, particularly if they have been immersed in the solution. The ulcers are not only annoying, but painful; and on their first appearance, if care is not properly taken to wash them in strong cyanide of potassium, and then in acid water, the operator will in a short time have to take a few days’ rest. We have repeatedly seen, by the aid of a magnifying glass, gold and silver reduced in these ulcerations. We have also known of eruptions breaking out over the bodies of workmen after inhaling those deleterious fumes when they were very bad, as when solutions were precipitated by acids, or being evaporated to dryness, in a close apartment, for the recovery of the metal. Repeatedly have the legs of workmen been thus afflicted, and always after they have been exposed to extra fumes.

The following statement of the general effects of electro-plating and gilding on the health of those engaged in these operations, as experienced

by ourselves and others who were with us, may not be uninteresting to our readers; but it is necessary to premise that the apartments in which we were employed were improperly ventilated.

The gas has a heavy sickening smell, and gives to the mouth a saline taste, and scarcity of saliva; the saliva secreted is frothy. The nose becomes dry and itchy, and small pimples are found within the nostrils, which are very painful (we have felt these effects in the nose from the hydrogen of the batteries where there were no cyanide solutions). Then follows a general languor of body, disinclination to take food, and a want of relish for food. After being in this state for some time, there follows a benumbing sensation in the head, with pains, *not* acute, shooting along the brow; the head feels as a heavy mass, without any individuality in its operations. Then there is bleeding at the nose in the mornings when newly out of bed; after that comes giddiness, objects are seen flitting before the eyes, and momentary feelings as of the earth lifting up, and then leaving the feet, so as to cause a stagger. This is accompanied with feelings of terror, gloomy apprehension, and irritability of temper. Then follows an occasional rushing of blood to the head; the rush is felt behind the ears with a kind of hissing noise, causing severe pain and blindness: this passes off in a few seconds, leaving a giddiness, which lasts for several minutes. In our own case the rushing of blood was without pain, but attended with instant blindness, and then followed with giddiness. For months afterwards a dimness remained as if a mist intervened between us and the objects looked at: it was always worse towards evening, when we grew very languid and inclined to sleep. We rose comparatively well in the morning, yet were restless, the stomach was acid, visage pale, features sharp, eyes sunk in the head, and the skin round them dark in colour: these effects were slowly developed. Our experience was nearly three years.

We have been thus particular in detailing these effects as a warning to all employed in the process; but we have no doubt that in lofty rooms, airy and well ventilated, these effects would not be felt. Employers would do well to look to this matter; and amateurs, who only use a small solution in a tumbler, should not, as the custom sometimes is, keep it in their bedrooms; the practice is decidedly dangerous.

PRACTICAL SUGGESTIONS IN GILDING.—According to the amount of gold deposited, so will be its durability: a few grains will serve to give a gold colour to a very large surface, but it will not last: this shews, however, that the process may be used for the most inferior quality of

gilding, and the fact that it is electro-gilt is no evidence as to quality. Gold thinly laid upon silver will be of a light colour, because of the property of gold to transmit light. The solution for gilding silver should be made very hot, say 200° Fah.; but for copper it should be at its minimum heat, 180° Fah. A mere blush may be sufficient for articles not subjected to wear; but on watch-cases, pencil-cases, chains, and the like, a good coating should be given. An ordinary sized watch-case should have from 20 grains to a pennyweight; a mere colouring will be sufficient for the inside, but the outside should have a good coating. A watch-case thus gilt, for ordinary wear, will last five or six years without becoming bare. We have known some to be in use full six years without losing their covering. Small silver chains, such as those sold at eight shillings, should have 12 grains; pencil-cases, of ordinary size, should have from 3 to 5 grains; a thimble from 1 to 2 grains. These suggestions will serve as a guide to amateur gilders, many of whom, having imparted only a colour to their pencil-cases, feel chagrin and disappointment upon seeing them speedily become bare: hence arises much of the obloquy thrown upon the process. Trinkets and jewellery, from being made of an alloy approaching gold in colour, have the merest blush of gold thrown over their surface.

UNEQUAL DECOMPOSITION AT ELECTRODE AND PROBABLE CAUSE.—

There is a general law laid down by electricians that there can be no inequality of decomposition in any part of an electrolyte, and that the amount of any element liberated at one electrode is, and must be, the exact equivalent of that which will be liberated at the other electrode. This law is correct in principle and in practice with simple compounds, such as a neutral protosalt, say of copper or iron; but should there be any excess of the solvent element, although that element may not act upon the positive electrode *per se*—such as if there be a little free sulphuric acid in a sulphate of copper solution, or in such solutions as the cyanides of gold and silver, in cyanide of potassium, as above described, and the batteries of weak intensity—there is always a tendency to unequal decomposition at the electrodes. And if the electro-metallurgist trusts the above law, without regard to the various circumstances stated, his solutions will be constantly liable to go wrong. To trace out the probable cause of this inequality led to the following experiments:—

1. A piece of zinc, measuring $2 \times 2\frac{1}{2}$ inches square, was amalgamated so that dilute sulphuric acid had no action upon it. This was put into a mixture of 1 sulphuric acid to 24 water, and surrounded with copper

placed as close to the zinc as would allow a free current of solution and escape of gas between them, so that the action of the acid upon the zinc would be as little retarded as possible when connection with the copper took place. They were kept in connection for one hour, when the zinc had lost in weight 97 grains, which was taken as a standard for the experiments.

2. The zinc and copper being again placed under the same circumstances, but an inch apart all round, and kept in connection by a strip of metal; for one hour the loss of zinc was 56·5 grains.

3. The copper and zinc were again put into the same position, and one inch apart; but instead of being connected by a strip of copper, they were connected with two copper electrodes of the same size—viz, $2\frac{1}{2} \times 2$ inches, which were put into a solution of sulphate of copper one inch apart (see Fig. 5). After being an hour in action, the zinc plate had lost 10·7 grains, the copper deposited was 9 grains. The question suggested by these results was, how many pairs of zinc and copper arranged for intensity would overcome the resistance of the one inch of copper solution, so as to give 56·7 grains in the hour.

4. The following table shews the result:—

One pair, zinc lost, . .	10·7; copper deposited, . .	9
Two pairs, „ . .	18 „ . .	17
Four pairs, „ . .	27 „ . .	26
Six pairs, „ . .	36 „ . .	34
Nine pairs, „ . .	45 „ . .	43
Twelve pairs, „ . .	53 „ . .	50
Fifteen pairs, „ . .	57 „ . .	55

We see from these experiments that when the zinc and copper are placed under the best circumstances, the chemical action induced by the contact is 97 grains per hour; but one inch of the solution in battery retards chemical action by the contact to the extent of 40·3 grains in 97, or 42 per cent.; and the addition of one inch of a solution of sulphate of copper retards the induced action 86·3 grains in 97, or 89 per cent. We have, therefore, been led to the conclusion that in the case of a weak battery power, that is, when the intensity is not sufficient to overcome all the resistance, so as to allow the full amount of induced chemical action to proceed, the positive electrode, where the resistance takes place, is in a certain state of electrical excitement over the negative electrode, inducing it to combine with any free acid, &c., that may be in contact with it; and this inducing excitement will be greatest when the battery is weak. Thus, in the above experiments,

when one pair of zinc and copper gave 56·7 alone, and the one inch of copper solution, being put in the current, only gave 10·7, the exciting or inducing tendency of the positive electrode was therefore equal to 46, while with nine pairs the inducing tendency was only 11·7; and we think it is this same tendency that in weak batteries causes more zinc to be dissolved in the battery than the equivalent of metal deposited in the decomposition cell; were the intensity of the battery increased, so that (taking our results as the standard) the full 97 grains were dissolved in the hour, there would be obtained an exact equivalent of decomposition in the whole course of the current. We are of opinion that this inducing tendency or electrical excitement of the positive electrode in the resisting electrolyte, when using weak battery power, is the cause and source of the undecomposing current of electricity passing through a solution, a phenomenon which has long been observed by electricians—a current sufficient to effect a galvanometer needle, but not to decompose the solution through which it passes, and which we think also produces the endosmose which every electrotypist must have observed, and which we will notice by and by.

In corroboration of these views, we will cite the following results:—

5. A battery of the same size of zinc plates as above—viz., $2 \times 2\frac{1}{2}$ inches—surrounded by copper placed 1 inch apart in sulphuric acid diluted with 24 parts of water; two copper electrodes of the same size were put into another vessel containing sulphate of copper, having in it a little sulphuric acid, the whole connected and kept in action for four hours; a piece of copper of the same size as the electrodes was put into the copper solution, but not attached to the battery. The following is the quantity of copper dissolved from the positive electrode more than was deposited upon the negative, which, according to the received law, should have been equal; no perceptible gas was evolved:—

With one pair battery dissolved 13 grains over equivalent.			
With two pairs	„	11	„ „
With four pairs	„	8	„ „
With six pairs	„	4	„ „
With nine pairs	„	2	„ „

The piece of copper put in the solution had lost nothing in weight during the four hours. One more experiment may be given: the battery plates of zinc and copper in acid measured 5×6 inches; acid, 1 sulphuric to 24 water. The decomposition cell was divided by a porous diaphragm of biscuit ware; into one division was put sulphate of copper, into the other the ordinary silver plating solution: two silver

electrodes, same size as battery plates, were used; the negative put into copper cell, the positive into silver. The quantity of copper deposited was taken as the equivalent of decomposing electricity passing: the action was sustained in each two hours. The loss given here is what was more than the equivalent of copper deposited, taking the equivalent of copper at 82, and of silver at 108.

With one pair battery the excess dissolved over equivalent was 70 grains.

With two pairs " " " " 30 "

With four pairs " " " " 12.5 "

With six pairs " " " " 0.6 "

A number of other experiments, varying in their conditions, gave similar results.

6. The next question was how far the size of the electrodes, in relation to the size of the battery plates, affected these results? The battery in these trials was excited, as in the other experiments, with 1 sulphuric acid to 24 water; the electrodes, copper in sulphate solution with a little free acid. The average of several experiments gave as percentage over the equivalent deposited—

Electrodes half size of battery plates, loss 15 per cent.

Electrodes same size " " 12 "

Electrodes double size " " 7 "

These experiments, we think, prove that in weak batteries there is an undecomposing current, sufficient to induce chemical action between the solvent and positive electrode, but not sufficient to pass through the intervening solution, between the electrodes, so as to cause a deposition upon the negative.

RESULTS OF EXPERIMENTS ON THE DEPOSITION OF OTHER METALS AS COATINGS.

COATING WITH PLATINUM.—This metal has never yet been successfully deposited as a protecting coating to other metals. A solution may be made by dissolving the metal in a mixture of nitric and muriatic acids, the same as is employed for dissolving gold; but heat must be applied. The solution is then evaporated to dryness, and a solution of cyanide of potassium added; next, it must be slightly heated for a short time, and then filtered. This solution, evaporated, yields beautiful crystals of cyanide of platinum and potassium; but it is unnecessary to crystallise the salt. A very weak battery power is required to deposit the metal: the solution should be heated to 100°. Great care must be taken to obtain a fine metallic deposit: indeed, the operator may not succeed once in twenty times in getting more than a mere colouring of metal over the surface, and that not very adhesive. The causes of the difficulty are probably these: the platinum used as an electrode is not acted upon; the quantity of salt in solution is very little; it requires a particular battery strength to give a good deposit, and the slightest strength beyond this gives a black deposit; so that when the proper relations are obtained, immediately after, the relations of battery and solution are changed, and the black pulverulent deposit follows: active motion assists in getting a coating.

We have occasionally succeeded in obtaining a bright metallic deposit of platinum, possessing the qualities of adhesion and durability: some of the articles thus covered presented no signs of change after many years; but we have never been so fortunate as to get a platinum deposit that could protect any metal from the action of acids, or other fluids by which the metal could be affected. We have covered iron, such as the end of a glassblower's blowpipe, so that it could be made red-hot without the iron rusting, but rather taking the characteristic appearance of platinum; but even that did not protect the iron from rusting when it was put a short time into water, or kept exposed to moist air. We have seen again and again recommendations of certain solutions of platinum for the purpose of obtaining a reguline metal, and no doubt

it has been obtained. M. Roseleur patented a process so early as 1846 for coating copper and its alloys with platinum. The solution of platinum he prepared thus:—To every 10 grains of platinum, made into chloride, as above described, and diluted with water, he adds a solution of 100 grains of phosphate of ammonia, which gives an orange-colour liquid. To this is added a solution of 500 grains of phosphate of soda, stirring well while this is being added. This liquid is boiled until all smell of ammonia ceases, and the solution begins to redden blue litmus paper, and becomes colourless, when the bath is ready for use. Iron, lead, zinc, or tin deposited platinum from this solution, so that these metals cannot be covered direct by the battery. By such solutions the patentee can deposit thick coatings of platinum; the colour of the metal thus deposited is grey, and requires to be brushed with iron-wire brushes, or polished with pumice stone; the colour of the metal, however, may be obtained by polishing with rouge and leather. Nothing is said as to the means of maintaining the strength of the solution. In 1847 M. Roseleur presented Louis Phillippe with a basin and ewer on which were deposited about 14 ounces platinum. Nevertheless, coating articles with platinum has never yet been made a branch of the electro-metal-lurgist's trade.

COATING WITH PALLADIUM.—Palladium is a metal very easily deposited. The solution is prepared by dissolving the metal in nitro-muriatic acid, and evaporating the solution nearly to dryness; then adding cyanide of potassium till the precipitate formed is dissolved: the solution is then filtered and ready for use. The cyanide of potassium holds a large quantity of this metal in solution, and the electrode is acted upon while the deposit is proceeding. Articles covered with this metal assume the appearance of the metal; but so far as we are aware, it has not yet been applied to any practical purpose. It requires rather a thick deposit to protect metals from the action of acids, which is probably the only use it can be applied to.

COATING WITH NICKEL.—Nickel is very easily deposited; and may be prepared for this purpose by dissolving it in nitric acid, then adding cyanide of potassium to precipitate the metal; after which the precipitate is washed and dissolved by the addition of more cyanide of potassium. Or the nitrate solution may be precipitated by carbonate of potash; this should be well washed, and then dissolved in cyanide of potassium; a proportion of carbonate of potash will be in the solution, which we have not found to be detrimental. A solution of sulphate of

nickel, neutralised by ammonia, is now largely used for coating articles with nickel, sufficient ammonia is added to keep the nickel in solution: this solution works well. Other solutions have been recommended; the following is the last we have seen. To a solution of 100 parts sulphate of nickel is added 14 parts caustic potash and 53 tartaric acid. We have articles coated with nickel from this solution of very great beauty, having a bright silver lustre, without scratch-brushing. Electrodes of nickel, cast into plates, are used, and may be purchased for that purpose. The metal is very easily deposited; it yields a colour approaching to silver, which is not liable to tarnish on exposure to the air. A coating of this metal is very useful for covering common work, such as gasaliers and other gasfittings, and even common plate. The property of not being liable to tarnish makes it eminently useful for all general purposes. We coated medals with nickel in 1845, which were exposed to the air for many years without tarnishing, and when last seen by us exhibited no change.

ANTIMONY.—This metal can be easily deposited from a chloride solution, made by taking equal parts of a saturated solution of salammoniac and muriatic acid, and putting into this a large pole of antimony connected with the copper of a battery, and the other pole, which may be of iron, in a porous cell filled with a little potash or soda solution placed in the same solution, similar to making silver solutions by the battery. Antimony has a bright white colour, not readily tarnished by exposure to the atmosphere: it is highly crystalline and brittle, which renders it of very little use to the electro-metallurgist. We notice it specially from a peculiarity which deposited antimony has, first noticed by George Gore, Esq., F.R.S. He says, "If during any part of the time the deposit is progressing, the deposited antimony be taken out and struck gently or rubbed with any hard substance, such as metal or glass, an explosion occurs, accompanied with a small cloud of white vapour, sometimes with a flash of light, and nearly always with considerable heat, sufficient to burn one's fingers, melt gutta percha, burn paper, and even scorch deal wood quite brown, especially if the deposit is thick, and invariably accompanied by fracture of the deposited metal. Sometimes, if the process of deposition has been interrupted and the deposited metal is not homogeneous, the fracture extends quite through the metal to upwards of one-eighth of an inch in depth." Mr. Gore mentions that these explosions sometimes take place in the solution by striking the deposit against the sides of the glass vessel containing the solution.

BISMUTH.—This metal may be easily deposited from a solution formed by dissolving the nitrate of bismuth in water containing a little nitric acid, sufficient to maintain it in solution. It requires a very weak battery power, and the electrodes kept considerably apart. The colour of the metal is white, with a red or pinkish tint, very pretty when newly deposited, very crystalline, and is of no known practical use to the electro-metallurgist. It is also subject to explode when struck with any hard substance.

CADMIUM.—A solution of cadmium is easily prepared by dissolving the metal in weak nitric acid, and precipitating it by carbonate of soda, washing this precipitate, and then dissolving it in cyanide of potassium; a battery power of three or four pairs is required, and the solution should be heated to at least 100° Fahr. The metal is white, and resembles tin; it is very soft, and does not present many advantages to the electro-metallurgist.

LEAD.—This metal may be deposited from a solution either of the acetate or nitrate, upon such metals as are electro-negative to it; but should a deposit be required on iron or zinc, then an alkaline solution must be used; this can be prepared by dissolving litharge in caustic potash or soda. The deposition of lead in a fine reguline condition requires careful management of the battery in relation to the metal solution, but its deposition is of no practical use.

IRON.—Iron may be easily deposited from a solution of ordinary copperas, using a very weak battery; still it is difficult to maintain the proper relations of battery and solution, so as to get a steady deposit of reguline metal with pure sulphate. Compound solutions have been found more suitable for this end. We have already, under "Stereotyping" (page 106), given an account of how thin coatings of iron may be got. The following, taken from the *Bulletin de la Société d'Encouragement*, gives the substance of the most successful operations in iron deposition. M. Klein, in a letter to Jacobi on the deposition of iron, after referring to a specimen which he had submitted for examination, goes on to say,—"In the experiments of which I now have the honour of giving you an account, my starting point was the known process of covering engraved copperplates with a coating of steel, which is quite successful in a bath composed of the chloride of ammonium and iron, to which I add a minimum quantity of glycerine. Nevertheless, all who have attempted coating with steel must have observed, when endeavouring to give

greater thickness to a very thin and brilliant layer of steel, that the surface cracks and the deposit detaches itself from the cathode in very brittle spangles. Other baths, composed in a uniform manner, and capable of being employed under the same conditions, must therefore be used. They may be classed under two categories, comprising baths composed of sulphate of iron and sulphate or chloride of ammonium. I first prepared three baths according to the formulæ $\text{FeOSO}_3 + \text{AmOSO}_3 + 6\text{HO}$, differing only in the manner of their preparation. The first bath consisted of a concentrated solution of crystals of the double salt $\text{FeOSO}_3 + \text{AmOSO}_3 + 6\text{HO}$, before mentioned. The second was composed of an admixture of a concentrated solution of each of these two salts, in the proportion of their equivalents. The third bath, which distinguished itself meritoriously from the others, was obtained by taking a solution of sulphate of iron, precipitating the iron by carbonate of ammonia, and dissolving the precipitate with sulphuric acid, thus avoiding all excess of acid. For the preparation of the baths in the second category I either mix solutions of sulphate of iron and chloride of ammonium in the proportion of their equivalents; or I dissolve in a solution of sulphate of iron, at a temperature of about 15° Reaumer (65° Fahr.), as much chloride of ammonium as it would take. All these baths were as highly concentrated and as neutral as possible. I used for an anode plates of sheet iron presenting a surface nearly eight times as large as that of the copper cathode. Upon the employment for decomposition of one of Daniell's cells, there were formed upon all the cathodes in the course of twenty-four hours irregular deposits full of cracks, which on the slightest attempt to remove them broke into a thousand pieces."

M. Klein mastered his difficulties by a long series of experiments, the details of which it is unnecessary to repeat, but he sums up the results of the quality of deposited iron thus:—"Galvanic iron, when first taken out of the bath, is as hard as cast steel, and very brittle; but when annealed at a temperature of dull redness, it loses much of its hardness and harshness. When further annealed to red heat it is malleable, and may be engraved as easily as soft steel. I am happy to say that, when made under favourable conditions and annealed uniformly and with the proper precautions, the electro deposits are not subject to twist, bend, or blister. There is no contraction, but, on the contrary, an almost imperceptible dilatation: this is of importance where the complete similarity of blocks is required, as their dimensions should receive no sensible alteration on being annealed."

In a paper read this year to the Physical Society by Mr. W. C.

Roberts, upon "the Electro-deposition of Iron," the author exhibited specimens which he had obtained by Klein's methods. The bath consists of a double sulphate of iron and magnesia, of specific gravity 1.155 (31° Twad.) The chief conditions of success is stated to be the neutrality of the bath and the employment of a very feeble current of electricity. Iron so obtained possesses a higher conductivity than any commercial iron, and has a specific gravity of 8.139. Galvanic iron has no permanent magnetism, but will receive magnetism like soft steel.

ALUMINIUM AND SILICIUM.—Attempts have been made to deposit the metals aluminium and silicium from their cyanide solution, as coating upon other metals, in the usual way. We have not ourselves tried any experiments upon these metals; but we take the following results of experiments from a paper by G. Gore, Esq., F.R.S., read to the Royal Society, who seems to have given the subject a good deal of attention:—

"It has long been known to chemists that all kinds of clay, stone, and sand, of which the earth is composed, consist of metals combined with oxygen, carbonic acid, sulphuric acid, and other non-metallic elements, forming therewith oxides, carbonates, sulphates, &c.; thus clay is an oxide of aluminium, sand an oxide of silicium, limestone a carbonate of calcium; but the separation of the metallic bases from the non-metallic elements with which they are combined has been a matter of so great difficulty, that few chemists have put themselves to the trouble of accomplishing it, and those who have done so have made use of the most powerful means and reducing agents, such as large voltaic batteries, potassium, &c., and have then obtained them in a state of alloy or combination with mercury. Sir Humphrey Davy, the discoverer of most of these bases, in his experiments on the decomposition of the alkalies and earths, used a powerful battery, consisting of 500 pairs of plates, and then succeeded in obtaining them combined with mercury, from which they were afterwards separated. Wöhler and Berzelius, in their discoveries of the means of separating the metals aluminium and silicium from their respective compounds, clay and sand, used a high temperature and potassium, and then succeeded in obtaining them in the condition of dull metallic powders, nearly infusible.

"By a means recently discovered, and described in the March number of the *Philosophical Magazine* for this year, I have succeeded in depositing the metals aluminium from clay, and silicium from sandstone, each in a perfect metallic condition, by dissolving pipe-clay, common red sand, pounded stone, &c., in various chemical liquids, and passing currents of electricity from ordinary small voltaic batteries through the solutions.

"My attention has since been directed to produce simple processes, whereby any person not possessing a knowledge of chemistry may readily coat articles with those metals, and thus cause the discovery to be immediately applied to human benefit in the arts and manufactures; and the following are the results of my experiments:—

"To coat articles of copper, brass, or German silver with aluminium, take equal measures of sulphuric acid and water, or take one measure each of sulphuric and hydrochloric acids and two measures of water; add to the water a small quantity of pipe-clay, in the proportion of 5 or 10 grs. by weight to every ounce by measure of water (or $\frac{1}{2}$ ounce to the pint); rub the clay with the water until the two are perfectly mixed, then add the acid to the clay solution, and boil the mixture in a covered glass vessel one hour. Allow the liquid to settle, take the clear, supernatant solution while hot, and immerse in it an earthen porous cell, containing a mixture of one measure of sulphuric acid and ten measures of water, together with a rod or plate of amalgamated zinc; take a small Smee's battery, of three or four pairs of plates, connected together intensity fashion, and connect its positive pole by a wire with a piece of zinc in the porous cell. Having perfectly cleaned the surface of the article to be coated, connect it by a wire with the negative pole of the battery, and immerse it in the hot clay solution; immediately abundance of gas will be evolved from the whole of the immersed surface of the article, and in a few minutes, if the size of the article is adapted to the quantity of the current of electricity passing through it, a fine white deposit of aluminium will appear all over the surface. It may then be taken out, washed quickly in clean water, and wiped dry and polished; but if a thicker coating is required, it must be taken out when the deposit becomes dull in appearance, washed, dried, polished, and re-immersed; and this must be repeated at intervals, as often as it becomes dull, until the required thickness is obtained. With small articles it is not absolutely necessary, either in this or the following process, that a separate battery be employed, as the article to be coated may be connected by a wire with a piece of zinc in the porous cell, and immersed in the outer liquid, when it will receive a deposit, but more slowly than when a battery is employed.

"To coat articles with silicium, take the following proportions: $\frac{3}{4}$ ounce, by measure, of hydrofluoric acid, $\frac{1}{4}$ ounce of hydrochloric acid, and 40 or 50 grains either of precipitated silica or of fine white sand (the former dissolves most freely), and boil the whole together for a few minutes, until no more silica is dissolved. Use this solution exactly in the same manner as the clay solution, and a fine

white deposit of metallic silicium will be obtained, provided that the size of the article is adapted to the quantity of the electric current: common red sand, or indeed any kind of silicious stone finely powdered, may be used in place of the white sand, and with equal success, if it be previously boiled in hydrochloric acid, to remove the red oxide of iron or other impurities.

"Both in depositing aluminium and silicium, it is necessary to well saturate the acids with the solid ingredients by boiling, otherwise very little deposit of metal will be obtained.

"Among the many experiments I have made upon this subject, the following are a few of the most interesting:—

"1. Boiled some pipe-clay in caustic potash and water, poured the clear part of the solution into a glass vessel, and immersed in it a small earthen porous cell, containing dilute sulphuric acid and a piece of amalgamated zinc; immersed a similar piece of bright sheet copper in the alkaline liquid, and connected it with the negative pole of a small Smee's battery of three pairs of plates, connected the zinc plate with the positive pole, and let the whole stand undisturbed all night; on examining it next morning I found the piece of copper coated with a white silver-like deposit of metallic aluminium.

"2. Obtained from a railway cutting in the town a small piece of the sand rock upon which Birmingham is built, boiled it in hydrochloric acid, to remove the red oxide of iron, washed it clean with water, and dissolving it by boiling in a mixture of hydrofluoric acid, nitric acid, and water; immersed in this solution a porous cell with dilute acid and zinc, as before; connected a piece of brass with the zinc by a wire, and suspended it in the solution, which was kept hot by a small spirit lamp beneath; after allowing it to proceed several hours, I found the piece of brass be-
metallic silicium.

"3. Took one part, by weight, of the sand purified by the hydrofluoric acid, and two an-
of potash, fused the mixture in a crucible
ceased, and a perfect mass formed; poured
and when cold, dissolved it in water, and used
manner as the former experiment, the action
hours, when a good deposit of metallic silicium

"4. Took some sand, washed it with the strong
macadamised, pounded it, and mixed it with a mixture
hydrochloric acid, to remove the red oxide of iron, and
dissolved it by boiling in a mixture of hydrofluoric acid, nitric acid, and water.

measure, of hydrofluoric acid, $\frac{1}{2}$ oz. of water, and $\frac{1}{2}$ oz. each of nitric and hydrochloric acids, until no more would dissolve; used the clear portion of this solution in the same manner as the former liquids, and readily coated in it a piece of brass with a beautifully white deposit either of aluminium or silicium. From these, and many other experiments which I have tried, it is quite clear that common metal articles may be readily coated with white metals, possessing similar characters to silver, from solutions of the most common and abundant materials, and thus bring within the purchase of the poorer classes articles of taste and cleanliness, which are at present only to be obtained by the comparatively wealthy."

TIN.—Tin is easily deposited from a solution of protochloride of tin. If the two poles or electrodes be kept about two inches apart, a most beautiful phenomenon may be observed: the decomposition of the solution is so rapid that it shoots out from the negative electrode like tentacula, or feelers, towards the positive, which it reaches in a few seconds: the space between the poles seems like a mass of crystallised threads, and the electric current passes through them without effecting further decomposition. So tender are these metallic threads, that when lifted out of the solution they fall upon the plate like cobweb. Seen through a glass, they exhibit a beautiful crystalline structure (see page 156). If a circular electrode of tin is used, and a small wire put in the centre of the chloride solution, the threadlike crystals will shoot out all round, and give quite a metallic conservæ. Tin may also be deposited from its solution in caustic potash or soda; but the ease and cheapness by which iron or copper can be covered with tin in the melted state has interfered much with any attempt to apply the battery process for that purpose, believing that, for such as tinplate, the operation would be expensive, and also next to impracticable. However, the deposition of tin upon iron has recently received a certain appearance of practical utility, by a process patented in 1872 by the late E. C. De Lobstein, of Paris, the principal novelty of which is, that after he has deposited a layer of tin he submits the article so coated to heat nearly sufficient to melt the tin, producing a frosted appearance. Several articles done in this way, seen by us, were very beautiful. The preparation of the tin solution is thus stated in the patent:—"My tin bath consists of 1000 parts of water, 22 acid, a half part of caustic soda, half a part of cyanide of potassium, and one quarter part of tin salt."

This patent has received notoriety from its being made the subject of a lawsuit, from the report of which we take the following account of

how the patentee operated on a large scale. The battery was composed of a lead vessel, 4 feet by 2 feet, and $7\frac{1}{2}$ inches deep: in the bottom was placed a copper sheet 4 feet 6 inches by 2 feet 4 inches, and above this, and resting upon small pieces of wood, was a zinc plate 3 feet 6 inches by 2 feet 3 inches. The exciting solution was made up with 8 lbs. 12 oz. acetate of lead, the same quantity of common salt, and 2 lbs. of sulphuric acid in as much water as filled the trough and covered the copper and zinc. The tinning bath was 8 feet long by 4 feet wide, and 4 feet deep, and contained 500 gallons of water, in which was dissolved 80 lbs. caustic soda, 2 lbs. 2 oz. cyanide of potassium, and 1 lb. 6 oz. salts of tin. There were tin electrodes attached to the copper of the battery, and the iron plates on which the coating of tin was made measured upwards of 160 square feet of surface. The result of the operation after being in action 4 days of 24 hours was—

	lbs.	oz.
Zinc dissolved in the battery, . .	1	$10\frac{1}{2}$
Tin dissolved from electrodes, . .	1	$15\frac{1}{2}$
Tin deposited upon the iron, . .	0	$12\frac{3}{4}$

We see in this experiment the large quantity of tin dissolved from the positive electrode, compared with the amount deposited upon the iron, corroborative of our remarks (page 175); also the large quantity of zinc dissolved for the work done, which is not surprising, considering the nature of the exciting liquid. With an ordinary battery of one pair zinc and copper, the zinc properly amalgamated, 1 lb. $10\frac{1}{2}$ oz. of zinc should deposit 4 lbs. tin; and, again, if it requires four days to deposit $12\frac{3}{4}$ oz., how long would it require to deposit 100 lbs.? or, taking the size of battery and vat here given, what space would be occupied by batteries and vats to deposit 100 lbs. tin per day—not an extraordinary quantity for the requirements of a manufactory of this sort?

DEPOSITION OF ALLOYS.—Many attempts have been made to deposit alloys of metals from their solutions. That two or more metals can be deposited together from a solution we have seen sufficient evidence; but the means to regulate the proportions of each, so as to make a thick coating, is a process very difficult, although we understand it is done very extensively by means not made public. The difficulty lies in getting a mixed solution of any two metals that are exactly equally decomposable; or, in other words, that the metals under the circumstances in which they are placed are exactly of equal conducting power:

otherwise the electric current will always travel through the one that offers the least resistance, and there will be none of the other metallic solution decomposed, or metal deposited, until the quantity of electricity is greater than the best conducting metal in the solution will allow to pass; then the other metal will be deposited in proportion to the extra electrical power that passes. As, for example, take a mixture of the cyanide of gold, silver, and copper in cyanide of potassium. The silver in this state is so much superior in its conducting power to the other salts, that all the silver may be deposited from the solution by a weak battery without any of the other metals; if the solution be afterwards heated, and the battery power kept so that no gas is allowed to escape from the articles, the gold may be deposited without any copper; but if the gas is allowed to flow from the article receiving the deposit, the copper will be deposited, and often more abundantly than the gold, as the escape of gas is not consistent with a reguline deposit of gold. We have thus deposited an alloy of gold and copper; we have also deposited gold and silver, but the alloy was very inferior and irregular. Alloys can be obtained of silver and palladium in cyanide solutions of zinc and copper from a solution of their sulphates; but in no instance have we found good alloys, or alloys that could pass as such in name or appearance. We have seen articles, made of iron, covered with copper and zinc in this manner, or in alternate layers, and the articles afterwards heated in charcoal, by which means a brass of fair appearance was obtained; but the process is attended with practical difficulty, and the product cannot be called deposited brass.

Several patents have been taken out for the deposition of alloys of various sorts. The following by Morris and Johnson embraces a wide range, and being well described, we will copy the specification:—

“This invention consists in the employment of solutions composed of cyanide of potassium and carbonate of ammonia, to which are added cyanides, carbonates, and other compounds of metals, in proportions according to the amount of deposit required to be made.”

In order that the invention may be fully understood and carried into effect, the patentees proceed to describe the means pursued by them as follows:—“These improvements consist in the employment of solutions composed of carbonate of ammonia (the carbonate of ammonia of commerce, or the sesqui-carbonate of ammonia of chemists) and cyanide of potassium, to which are added carbonates, cyanides, or other compounds of metals in various proportions. For the well-known alloy brass, carbonate of ammonia and cyanide of potassium are used in the following proportions—viz., to each or every gallon of water are added

1 lb. of carbonate of ammonia, 1 lb. of cyanide of potassium, 2 oz. of cyanide of copper, and 1 oz. of cyanide of zinc : these proportions may be varied to a considerable extent. Or the patentees take the before-named solution of carbonate of ammonia and cyanide of potassium, in the proportion of 1 lb. of each to 1 gallon of water ; and they take a large sheet of brass of the desired quality, and make it the anode or positive electrode, in the aforesaid solution, of a powerful galvanic battery or magneto-electric machine, and a small piece of metal, and make it the cathode or negative electrode, from which hydrogen must be freely evolved. This operation is continued till the solution has taken up a sufficient quantity of the brass to produce a reguline deposit. The solution may be used cold ; but it is desirable, in many cases, to heat it (according to the nature of the article or articles to be deposited upon) up to 212° Fah. For wrought or fancy work about 150° Fah. will give excellent results. The galvanic battery, or magneto-electric machine, must be capable of evolving hydrogen freely from the cathode or negative electrode, or article attached thereto. It is preferred to have a large anode or positive electrode, as this favours the evolution of hydrogen. The article or articles, treated as before described, will immediately become coated with brass : by continuing the process any desired thickness may be obtained. Should the copper have a tendency to come down in a greater proportion than is desired, which may be known by the deposit assuming too red an appearance, it is corrected by the addition of carbonate of ammonia, or by a reduction of temperature when the solution is heated. Should the zinc have a tendency to come down in too great a proportion, which may be seen by the deposit being too pale in its appearance, this is corrected by the addition of cyanide of potassium, or by an increase of temperature.

“The alloy German silver is deposited by means of a solution consisting of carbonate of ammonia and cyanide of potassium (in the proportions previously given for the brass), and cyanides or other compounds of nickel, copper, and zinc in the requisite proportions to constitute German silver ; it is, however, preferred to make the solution by means of the galvanic battery or magneto-electric machine, as above described for brass. Should the copper of the German silver come down in too great a proportion, this is corrected by adding carbonate of ammonia, which brings down the zinc more freely ; and should it be necessary to bring down the copper in greater quantity, cyanide of potassium is added—such treatment being similar to that of the brass before described.

“The solutions for the alloys of gold, silver, and other alloys of

metals are made in the same manner as above stated, by employing anodes of the alloy or alloys to be deposited; or by adding to the solutions the carbonates, cyanides, or other compounds, in the proportions forming the various alloys: always using, in depositing, an anode of the required alloy. These solutions are subject to the same treatment and control as those of the brass and German silver before described.

"The patentees claim the combination of the carbonate of ammonia before named, or other carbonates of ammonia and cyanide of potassium, as the ingredients for their solutions for depositing alloys of metals."

The expense of depositing common metals will remain a barrier to the use of electro-metallurgy in making such alloys as brass, a consideration which some patentees do not seem to consider. We have the following given as methods for mixing up solutions for depositing brass which will prove our position.

As an illustration of this invention we take the patentee's method of depositing a coating of brass by galvanic agency, in which he employs the following:—1. "A solution of the double chloride of zinc and ammonia. 2. A solution of the double chloride of zinc and potassium, 3. A solution of the double chloride of zinc and sodium. 4. A solution of the double acetate of zinc and ammonia. 5. A solution of the double acetate of zinc and potassium. 6. A solution of the acetate of zinc and soda. 7. A saturated solution of carbonate of zinc and carbonate of ammonia. 8. A solution of the double tartrate of zinc and of potash, soda, or ammonia. (To one thousand parts of the solution of tartrate of zinc, indicating three degrees on the salinometer, thirty parts of hydrochlorate of ammonia and eighty parts of hydrochloric acid must be added.) 9. A solution of citrate of zinc rendered soluble by an excess of citric acid. 10. A solution of tartrate of zinc in potash or soda. With each of the above solutions an analogous solution of copper must be mixed in the proportion suitable for obtaining the required depth of colour."

It is recommended that a battery of sufficient strength be used as will be capable of evolving hydrogen; to do this for most of the solutions named will require several pairs; but taking the cost at the lowest, and that only one pair of plates be used in the battery, and suppose we deposit 3 lbs. of yellow metal—

There are dissolved in battery 3 lbs. zinc @ 6d.,	= 1s. 6d.
Dissolved from electrode to supply copper, 2 lbs. @ 1s.,	= 2s. 0d.
Dissolved from electrode to supply zinc, 1 lb. @ 6d.,	= 6d.

4s. 6d.

Which will make the one pound 1s. 4d. for the metals used, not including solutions, &c. This alloy can be purchased at 1s. If several pairs of battery have to be used, the zinc has to be multiplied by the number of pairs: so that if four pairs are used, the cost of zinc for battery power will be 6s. instead of 1s. 6d. Nevertheless, were such alloys capable of being deposited in any given proportion regularly, even this cost would not be against their use for many purposes. We take the following from the "*Progress of General Science*, Vol. II."

"The following solutions of different metals are given by Brunel, Bisson, and Gangain, as being capable of giving a deposit of bronze (brass?):—

- 50 parts Carbonate of potash.
- 2 " Chloride of copper.
- 4 " Sulphate of zinc.
- 25 " Nitrate of ammonia.

"A bronze plate is used as the positive electrode. The deposit given by this solution has been seen by Becquerel, who mentions that it bears comparison with any ordinary bronze in appearance." A solution of the above materials in water strikes the ear as somewhat hypothetical: that a mixed solution of copper and zinc will give, under certain conditions, a compound deposit we know, and also that, with a quantity of other salts present, will give peculiar tints of colour, a circumstance which may be obtained without a compound deposit. But the difficulty to be overcome is to proportion the deposit of different metals, so that we may make up a solution and battery that will deposit either Muntz's yellow metal, Stirling's yellow metal, gun-metal, or common brass at pleasure, and that we may be able to produce compounds that are constant and unvarying: so that, for example, we could deposit silver or gold of the standard quality, all which, notwithstanding the many statements that have been made in print, have yet to be discovered.

Besides the ordinary electro-metallurgical operations, the public are from time to time told through the press that electricity has been applied to the extraction of metals from their ores: but on examination the statement is invariably found to be incorrect, the metal being in all cases separated from the ore by means of an acid or acids, and the electro-metallurgical operations not applied till after this separation takes place, so that its application is altogether apart from and is not applied until after the metal is extracted from the ore. Such an application for common metals is *commercially* absurd; and nothing can exhibit the want of practical consideration so much as some of the patents taken out

for this object. The greater number of these patents are intended for copper ores, upon which we will offer a few remarks. It will be seen from the principles of deposition that, supposing the copper was all in solution to be deposited by a battery, the cheapest form known will give the loss of one ton of zinc and sulphuric acid to get one ton of copper, which would be upwards of £20 for the materials destroyed, while a ton of copper may be smelted by the ordinary process for half that sum. We give the following extract of a patent as an illustration, not because it is worse than others, but it is more definite in its methods and battery than most of these patents, and the patentee was an excellent electrician.

"Mr. Andrew Crosse, of Broomfield, the electrician, has just specified his patent for improvements in the extraction of metals from their ores. The apparatus employed for this purpose consists of a wooden or earthenware vessel, capable of holding from 250 to 300 quarts, at a short distance above the bottom of which is a movable platinum frame, covered with a netting of platinum wire, the meshes being about 1 inch each way. This frame is connected to the positive pole of a Daniell's battery by a platinum wire, covered with a non-conducting material throughout those parts of it exposed to the liquid in the vessel; the negative pole of the battery being connected to a copper wire, from which is suspended by three smaller wires, in the interior of the vessel a bowl of wood lined with sheet copper, and covered with a copper-wire netting. The battery in connection with the apparatus should consist of 20 pairs of plates, each in a gallon glass vessel, filled with a saturated solution of sulphate of copper, to which has been added from 1-20th to 1-10th part of sulphuric acid.

"The mode of operating is as follows:—The vessel is partially filled with water acidulated with sulphuric acid—230 quarts of water and 5 quarts of sulphuric acid being a convenient quantity. About 15 lbs. of the copper ore, previously calcined and reduced to powder, is then stirred into the liquid in the vessel and allowed to subside, after which the platinum frame is lowered on to the surface of the ore, and the copper-lined bowl suspended in its place, when the electric current immediately begins to act; but it is preferred to allow the ore to remain four or five days in the acidulated water before applying the electric current. The liquid during the process should be kept heated even as high as the boiling point, by which the separation of the copper and its deposition in the bowl will be facilitated. The time occupied in effecting this is generally three or four days, when the whole of the copper is removed; the acid liquid and sediment, which will contain any other

metals that may have been present, are run out through a plug-hole in the bottom of the vessel. The sediment should be tested to ascertain if it still contains any proportion of copper; and if so, it can be mixed with fresh calcined ore, and again operated on; the liquid does not require any fresh quantity of acid to be added to it during the process, and afterwards it may again be similarly used."

Here we have 20 pairs of plates recommended to be used in the battery, making a destruction of 20 tons of zinc and acid for one ton copper, and taking four days to deposit; and at the ordinary percentage of ore to get this, there will have to be 300 tons of ore operated upon, requiring acres of tanks, heated according to specification, independent of the furnace for calcining. Having got the ore calcined and free of sulphur, it would be preferable to fuse it with carbonaceous matters and get the copper direct. Notwithstanding the commercial absurdity of all these applications and patents, still there are several ingenious adaptations worthy of the attention of the electro-metallurgist as a study in his profession.

ELECTRO SMELTING.—We have also to rank a proposition of our own among the absurd patents taken out for the extraction of copper from its ores by electricity. In the early history of the art, application was made to our employers to try if the process of electro-deposition could not be applied to the extraction of the copper from the water issuing from the copper mines and large heaps of ore accumulated round the mouth of the mines on the Island of Anglesea, apparently a very legitimate application, and thither we went with batteries, and all other necessary appliances. The process by which the copper at that time was obtained from the waters was by adding metallic iron, on which the copper was precipitated. One ton of iron should theoretically precipitate one ton of copper; but in practice it required ten tons of iron to obtain one ton of copper. To put into this solution an electrode of copper, and attach a battery to it, and deposit the copper from the solution, seemed a very easy and simple affair; but to our surprise, instead of a deposit the copper electrode was rapidly dissolved, and no deposition took place till after a considerable time had elapsed, and the solution had become of a blue colour; then deposition went on rapidly, and continued until the water was completely exhausted of copper; but the quantity of zinc dissolved in the battery was ten times the amount of the copper got from the waters, and consequently much more expensive than the ordinary process with iron. After some investigation, we found the cause to be from the water containing a large quantity of persulphate

of iron, so that when the metallic iron was put into this solution no copper was deposited until all the persulphate of iron was reduced to the protosulphate, thus—

Persulphate of iron is composed of two iron and three acid.	{	Iron.....	—————	protosulphate of iron.
		Iron.....	—————	protosulphate of iron.
		Sulphuric acid	—————	
		Sulphuric acid	—————	
Metallic iron,	{	Sulphuric acid	—————	
		Iron.....	—————	protosulphate of iron.

After this reaction the copper in the water is replaced by the metallic iron remaining, thus—

Sulphate of copper is composed of one copper and one sulphuric acid.	{	Copper.....	—————	metallic copper.
		Sulphuric acid	—————	
		Iron.....	—————	protosulphate of iron.

When the copper electrode was put into the copper waters the same reaction took place between the copper and persulphate of iron—the copper was dissolved by the persulphate, and no deposition by the battery took place until all the iron was reduced to the state of protosulphate. And then all the copper thus dissolved, as well as that originally held in solution, had to be deposited by the battery, and that at the expense of the zinc, which was, as stated, ten times the amount of the copper that had been originally in the water.

It was during this visit to the Anglesea mines that we first saw copper smelted from the ore; and seeing the ore in the fused condition, the question occurred to us, may not the battery be applied to the fused liquid, and deposit the copper upon an electrode less fusible?

The experiment was tried in a quantity of ore fused in a crucible, using iron electrodes, and we obtained a favourable result. A patent was applied for, notice of which was soon circulated, under the heading of smelting copper by electricity; and ere it went the round of the newspaper press its value was magnified to the extent that the saving of coal alone was calculated at half a million of money, and the copper was to be so cheap, that if the same money value was to be retained in the coins, the penny piece would require to be the size of butter plates; and long after we had found out our error, a premium was offered for any

one who would introduce the process into France, and Messrs. Phillips and Rives were appointed by a learned society in Paris to investigate the process. Our results in the crucible and elsewhere were a mere substitution of iron for copper, which was practically of no utility, and the electricity applied was of no use. However, many curious phenomena were observed in our experiments, which do not fall within our present inquiry.

We have thus given a brief review of the practical operations of electro-metallurgy for the guidance of the student, who, as he proceeds, will find that the difficulties which at first beset his path will gradually disappear: easier modifications of processes will suggest themselves, as all operators cannot with equal facility follow the same directions. New facts will reveal themselves to his inquiries; a wide field of interesting and profitable research will open up before his mind, and the steady and persevering experimenter and observer will not fail to reap an abundant harvest of honour and gratification, in being an instrument in promoting the knowledge of the working of the laws of Nature; and although thirty-five years have passed since the art of electro-metallurgy first began, much has yet to be discovered, and these remarks remain as applicable now as in our first edition twenty-five years ago.

ELECTRICAL ENDOSMOSE.—When working with weak batteries in the varied circumstances under which electro-metallurgy is conducted, there have been many phenomena observed of great importance in the study of dynamic electricity, some of which we have already noticed—such as the non-transfer of the positive element of an electrolyte, and also that the electrodes are in a state of electrical tension or excitement, in relation to bodies round them, in a similar manner to a substance charged with statical electricity, which is manifested by extra chemical action at the positive pole. There is also another phenomenon which the electro-metallurgist will not have failed to observe when operating with porous cells or diaphragms, that the liquid in one cell or division increases in bulk and the other decreases. This is termed endosmose, and depends, we think, on a weak undecomposing current passing through an electrolyte. The late Professor Faraday says, in his *Electrical Researches*, that a current of electricity may be made to pass through solutions without decomposing them. Also, the late Mr. Sturgeon gave

it as his opinion that there was always an undecomposing current passing with the decomposing. Jacobi says, "The current from a single pair does not decompose water, and yet produces deflection of the galvanometer. If the current of a ten-pair battery be weakened by the interposition of a long thin platinum wire to such a degree that it produces the same deflection as the current of a single pair, it will behave towards water in the same manner without decomposing it."

These views have forced themselves upon us as the result of long experience, and we think that the undecomposing current is greatest when the decomposition is least, and that endosmose, which is of two sorts, namely, a flow of the salt in solution from one cell to the other, and a flow of water: the latter alters the bulk of the solutions, the former does not, and is invisible to the eye; the effect of these undecomposing currents varies with the strength of the battery, or otherwise, the resistance offered to the passing of the electric current by the electrolyte. To make this matter a little more plain, we select a few experiments as illustrations. When a plate of zinc and copper are put into dilute acid, and the two connected by a slip of copper, as Fig. 50, the electricity passes from the zinc in the solution, and through the solution to the copper, when it flows back to the zinc by the connection



Fig. 50.

a. Suppose we call the quantity of electricity flowing from one metal to another in these circumstances 100; then if this free flow of the current of electricity be interrupted by an electrolyte, thus (Fig. 51), the current generated in the battery cell flows from the copper *c* of the battery, to the electrode *d*, through the electrolyte solution to the electrode *e*, and back to the zinc *z*; but the electrolyte does not allow the flow of electricity to pass through it with the same ease as the metallic copper, having work to do in decomposing the salt; but the amount of electricity in a given time from the battery, without an intervening electrolyte, being 100, and the work done in the electrolyte in the same time be only 50, then the tension of the electrodes inducing an undecomposing current, chemical action upon the positive electrode, endosmose, &c., is equal to 50. Suppose the work done in the electrolyte be only 20, then these phenomena by the undecomposing current will be 80; but should the work done be 80, then the influence of the undecomposing current will

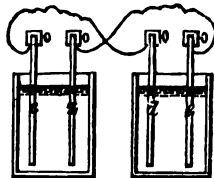


Fig. 51.

be represented by 20. These figures only express the principle of the

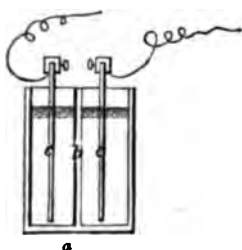


Fig. 52, *a*, the cell; *b*, porous partition; *c, c*, copper electrodes.

two kinds of work done, which will be more manifest by the experimental results. Endosmose can only be observed when working with porous cells, where the decomposing or electrolyte solutions are divided by a porous partition. The following experiment was with a separate battery, and the decomposing cell divided by a porous partition, as Fig. 52. In each division of the cell *a*, was put a solution of 500 grains of sulphate of copper, the two solutions were at one level, the battery had 9 pairs of zinc and copper in dilute

sulphuric acid, 1 to 24. The current was continued until the liquid in the negative division was completely exhausted of copper, requiring about 60 hours. The liquid in this cell had increased 4 oz. by measure, or 20 per cent.; the solution in the positive cell had lost 6 oz. This cell contained all the sulphate of copper originally held in the two; the electrode had lost in weight 257 grains; the negative electrode had gained in weight 250 grains. In this experiment we see that all the sulphuric acid in the negative cell has been transferred to the positive by electrolysis, that 500 grains of the salt, undecomposed, has been carried from the positive to the negative division, besides 4 oz. of water carried in the same direction, which took place principally during the latter part of the experiment, when the negative division became exhausted. This and similar experiments were repeated many times, with different strengths of battery, and with similar results.

In the next experiment, Fig. 53, *a* is a glass vessel filled with water,

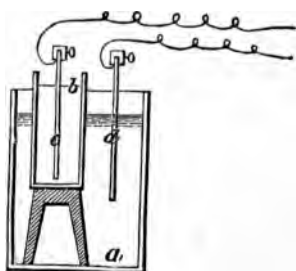


Fig. 53.

acidulated with muriatic acid, 1 to 24, in which is placed *b*, a porous vessel containing 100 grains of sulphate of copper in solution, in which is placed the negative pole, *c*, the solution measuring 4 oz. The current from a four-pair battery was kept up till the solution in porous vessel was exhausted of copper—there were 25.1 grains copper deposited: the liquid now measured $4\frac{1}{2}$ oz., and contained a mere trace of chlorine; the

positive electrode, *d*, had lost 182 grains; the liquid at the bottom of the vessel was blue, and contained all the sulphuric acid that was in the porous vessel. Here again we have endosmose of water, no transfer of metallic element, and a large quantity of copper dissolved from the positive electrode. The battery plates were large, 6 by 8 inches, and the resistance of the electrolyte was considerable.

Another experiment where resistance was increased, see Fig. 54; *a*, a glass vessel filled with distilled water; *b*, porous vessel with solution of sulphate of copper, with negative electrode, *d*; *c*, porous vessel with hydrochloric acid, 1 to 24 water, with positive electrode *e*; battery used was nine pairs of zinc and copper, each of the porous vessels had 4 oz. solution. After 18 hours the results were—negative electrode had deposited upon it 26 grains copper; solution not exhausted of copper and had increased in bulk $1\frac{1}{4}$ oz., and did not contain a trace of muriatic acid; the positive electrode was covered with a white powder, and had lost in weight 37 grains; the liquid had lost $\frac{3}{8}$ ounce in bulk, and contained a considerable portion of sulphuric acid. The water in glass vessel was tinged blue, and had both sulphuric and hydrochloric acids in it, and had lost in bulk $1\frac{1}{2}$ oz.

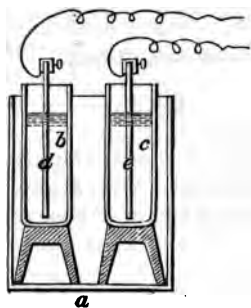


Fig. 54.

Here again we have an increase of bulk by endosmose in the negative cell, a loss in the positive, and a transfer of the sulphuric acid through the layer of distilled water to the positive, which contained sulphate of copper.

These and a number of other experiments suggested to us the opinions, already given, that during electrolysis only the element in combination with the metal is transferred from electrode to electrode—the metallic element is not; and that besides the decomposing current there is an undecomposing current, which carries with it, when the resistance is not great or the decomposing current is great, a quantity of the salt in solution, without water, and which does not increase the bulk, but when the decomposition is little it carries with it water, which increases bulk. To test this last idea we tried the following experiment (Fig. 55):—*a*, a glass vessel divided by a porous partition, *b*, each division filled with water to the lip. In one division was placed a zinc plate, *z*; in the other a copper plate, *c*, each plate being 4 by 6 inches square,

connected by a slip of copper, *d*. The glass vessel had a spout with a small vessel, *e*, under, to catch any overflow. The current passing was sufficient to effect a not very delicate galvanometer needle, but there was no apparent decomposition. This apparatus was kept in action for forty days, always keeping the solution in the zinc division to the proper level. In this way 32 oz. of water passed through the porous partition, and were caught in the vessel *e*, not taking into account loss by evaporation. The zinc plate had oxidised upon the surface, which, being dissolved off,

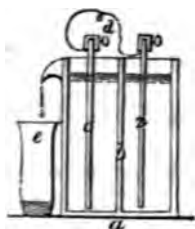


Fig. 55.

showed a loss of 32 grains. Each division of the glass vessel held 20 oz. liquid. With two copper electrodes, one in each division, connected with a battery of nine pairs of equal-sized plates with the electrodes, the flow of water was on an average 2 oz. per day.

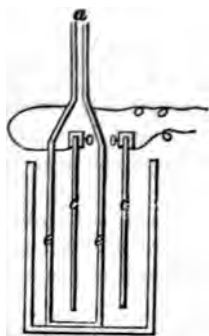


Fig. 56.

In order to see if it would sustain any pressure, the apparatus was fitted up as Fig. 56, *a* being a $\frac{1}{4}$ -inch tube 12 inches above the level of liquid. The tube was widened at bottom and joined to the mouth of the porous cell *e*; *c c* are two electrodes connected with a nine-pair battery. The water flowed up the tube and ran over with the same ease as it did over the spout of glass vessel. This experiment suggested to us the probability that some such electrical influence may be at work in raising the sap from the earth up through the vessels of vegetables, even of the highest trees, although the quantity of liquid in these experiments is comparatively small to that passing along the vessels of a tree in leaf. Still, in some of our experiments, with electrodes measuring only 3 by 2 inches, we had an increase of 1 oz. in twenty-four hours. Had the larger plates or electrodes given the same proportions, we should have had 4 oz. transferred in the twenty-four hours, instead of 2 oz.

THEORETICAL OBSERVATIONS.

WE have described at considerable length the practical details connected with the art of electro-metallurgy, without pausing to inquire into the philosophy of the action of the electric currents by which the effects are produced. It will be unnecessary to enter into a long discussion of the numerous theories that have been advanced from time to time to explain the action that takes place in a battery or decomposing cell, while the current is passing through the solution—a brief reference to the more commonly received opinions will be sufficient for the present purpose.

ACTION OF SULPHATE OF COPPER ON IRON.—In order to convey our ideas accurately, let us suppose that the solution undergoing decomposition is sulphate of copper. This salt is composed of sulphuric acid and copper, which may be represented as $\text{SO}_4 + \text{Cu}$: these are held together by what is known as chemical attraction or affinity; but if iron is put into the solution, the combination of the acid and copper will be overcome by the attraction of the acid to the iron, for which it has a stronger affinity than for the copper. Hence iron put into sulphate of copper decomposes it, thus :—

Sulphate of copper	{	sulphuric acid		sulphate of iron.
composed of	{	copper		copper metallic deposited.
Iron metallic	{	iron		

Were we to put a piece of copper into a solution of sulphate of copper, there would be no action, the forces being equal; but if by any means we were to communicate to this piece of copper a higher attractive force for the SO_4 than that of the copper which is already in union with it, we should cause the acid to leave the copper it was originally combined with, and to combine with the new piece of copper. Bearing these general principles in view, we shall proceed to state the different opinions of the most eminent electricians on this subject.

FARADAY'S THEORY OF ELECTROLYSIS.—The late Professor Faraday

says in his *Researches* — “Passing to the consideration of electrochemical decomposition, it appears to me that the effect is produced by an *internal corpuscular action*, excited according to the direction of the electric current, and that it is due to a force either *superadded to*, or *giving direction to*, the *ordinary chemical affinity* of the bodies present. The body under decomposition (say sulphate of copper) may be considered as a mass of acting particles, all those which are included in the course of the electric current contributing to the final effect; and it is because the ordinary chemical affinity is relieved, weakened, or partly neutralised by the influence of the electric current in one direction parallel to the course of the latter, and strengthened or added to in the *opposite direction*, *that the combining particles* have a tendency to pass in opposite courses.

“In this view the effect is considered as *essentially dependent* upon the *mutual chemical affinity* of the particles of opposite kinds. Particles *aa* could not be transferred or travel from one pole N, towards the other pole P, unless they found particles

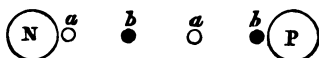


Fig. 57.

of the opposite kind, *bb*, ready to pass in the contrary direction; for it is by virtue of their increased affinity for those particles, combined

with their diminished affinity for such as are behind them in their course, that they are urged forward.

“I conceive the effects to arise from forces which are *internal*, relative to the matter under decomposition, and not *external*, as they might be considered, if directly dependent upon the poles. I suppose that the effects are due to a modification by the electric current of the chemical affinity of the particles through or by which that current is passing, giving them the power of acting more forcibly in one direction than in another, and consequently making them travel by a series of successive decompositions, in opposite directions, and finally causing their expulsion or exclusion at the boundaries of the body under decomposition, in the direction of the current, *and that in larger or smaller quantities*, according as the current is more or less powerful.”*

In the above figure, the particles *aa* may be termed copper Cu, and the particles *bb* sulphuric acid SO₄, which will enable us to follow the comparison of the different views.

GRAHAM'S THEORY OF ELECTROLYSIS.—The late Professor Graham

* Faraday's *Experimental Researches*, vol. I., paragraphs 518, 519, 524.

supposed that the compound particles, such as sulphate of copper, possess polarity, so that the particles in the battery or decomposition cell will stand in relation to each other in a polar chain, as in Fig. 58.



Fig. 58.

He then represented electrotyping by the porous cell system, as follows:—

“The liquids on either side of the porous division may also be different, provided they have both a polar molecule. Thus, in Fig. 59, the polar chain is composed of molecules of hydrochloric acid, extending from the zinc to the porous division at *a*, and of molecules of chloride of copper from *a* to the copper plate. When the Cl of molecule 1 unites with zinc, the H of that molecule unites with the Cl of molecule 2 (as indicated by the connecting bracket below); the H of molecule 2 with the Cl of molecule 3; the Cu of molecule 3 with the Cl of molecule 4; and the Cu of this molecule being the last in the chain, is deposited upon the copper plate. Dilute sulphuric acid in

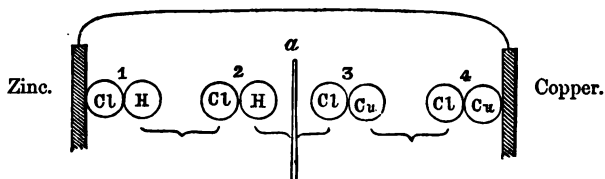


Fig. 59.

contact with an amalgamated zinc plate, and the same acid fluid saturated with sulphate of copper in contact with the copper plate, are a combination of fluids of most frequent application.”*

According to this theory, all the particles between the zinc and copper during the action of the batteries will be performing a whirling motion; for when the Cl of molecule 1 is liberated, the H of 1 will combine the Cl of 2, which compound molecule must whirl round to be in its proper polar position, which will necessitate that interchange distinctly referred to by Professor Faraday—a mutual transfer of the elements; the Cl will pass towards the zinc plate, and the H and Cu towards the copper plate.

DANIELL'S AND MILLER'S VIEWS.—A similar theory was given by the late Professor Daniell in his *Chemical Philosophy*; but, as already stated

* Graham's *Elements of Chemistry*, second edition, 1869.

in page 39. he, in conjunction with the late Professor Miller, communicated to the Royal Society an account of a series of experiments, from which they came to the conclusion that there was not a mutual transfer of the elements of an electrolyte, as all previous theories had necessitated. They nevertheless came to the conclusion that the positive elements in certain salts were transferred in given proportions—that potassium from sulphate of potash was transferred at the rate of one-third of an equivalent, barium from nitrate of barytes at one-sixth of an equivalent, and magnesium from sulphate of magnesia at one-twelfth of an equivalent; and conclude with the following remarks:—

“These facts are, we believe, irreconcilable with any of the molecular hypotheses which have been hitherto imagined to account for the phenomena of electrolysis, nor have we any more satisfactory at present to substitute for them; we shall therefore prefer leaving them to the elucidation of further investigations to adding one more to the already too numerous list of hasty generalisations.”*

There were certainly great difficulties in reconciling the results which they obtained had they been the effect of electrolysis, as these eminent chemists considered; but in this, we think, they were in error, and that the transfer of potassium, barium, and magnesium which they obtained was not by electrolytic action, but electrical endosmose. The result of our experience is, that when two different kinds of liquids are separated by a porous partition, there is a certain amount of transfer or mixing of the two liquids, either by what is termed ordinary endosmose, caused by one of the liquids being of greater specific gravity, or by what the late Professor Graham called diffusion; but besides these, and controlling these in ordinary salts, when an electric current is made to pass through these solutions from a galvanic battery, there is a flow of the solution in the line of the electric current without decomposition; and this takes place as easily when both divisions are filled with the same solution as when they have different salts in solution and independent of their specific gravity. And it was, we think, this flow that led Daniell and Miller to the supposition that the metallic elements of different salts were partially transferred by electrolysis. We believe that in no case of electrolysis by the battery is the metallic element of the electrolyte transferred or transmitted from the positive electrode to the negative.

Notwithstanding the experiments and conclusions come to by Professors Daniell and Miller, published in the *Philosophical Transactions* for 1844, and our own experiments and conclusions, published in the

* *Philosophical Transactions*, Part I. for 1844.

Chemical Society's Journal in the same year, the old theory of electrolytic action and mutual transfer is still given as the true one in books and periodicals, by philosophers of high standing. It is no doubt difficult to give up an old and generally received theory, especially when it agreed with a cherished dogma of there being two electricities passing from electrode to electrode exactly equivalent in force, whether these forces acted according to Faraday's or Graham's suppositions, or as given by others. To be more in keeping with the dogma, a is the electrode attached to the copper of battery; b is the electrode attached to zinc of battery; CCCC and SSSS represents a solution of sulphate of copper, as a chain of particles between the two electrodes. Electricity by the dogma is a compound force composed of

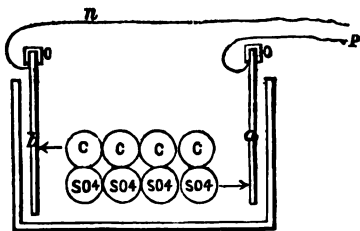


Fig. 60.

resinous and vitreous electricities, or negative and positive. When they are separated by any means they have a strong attraction for each other, so that when two substances are charged with the different kinds of electricity, they have an attraction for each other, and if easily moved will rush together; but two substances charged with the same kind of electricity repel each other. In the double chain of sulphate of copper in the above figure, the copper, C, is the positive element in the chain, and SO_4 is the negative element. The positive electricity coming from the battery by the wire p , the electrode, a , gets charged with that kind of electricity; while the negative electricity from the battery is simultaneously passing through the wire n , charging the electrode with negative electricity. The positive electrode a therefore repels the positive element C, and attracts the negative element SO_4 ; and the negative electrode simultaneously attracts the positive C, and repels the negative SO_4 : so that there is a mutual play of forces. This explanation of the action of the current in decomposing the electrolyte, like the two others given, necessitates a mutual transfer of both positive and negative elements in equal proportions, as the one electric force is exactly the equivalent of the other, which, as has been proven, is not the fact. We must therefore seek for some other explanation, and in doing so disregard for the time the dogma of two electric currents passing through an electrolyte in different directions. We are more inclined to think that dynamic electricity is a simple force passing

through a conducting chain from the zinc of battery through the conducting element of the solution of battery to the copper, thence by the wires and the conducting element of the electrolyte, and back to the zinc and solution in battery.

PROPOSED THEORY.—Having carefully considered the various phenomena attending electrolysis, in the decomposition of metallic salts, we think that the electricity is conducted through the solution by the base or positive element in the electrolyte, which it does as if it were a solid chain of particles or wire. We have already said, that if to a solution of sulphate of copper we add a piece of iron, the acid in union with the copper will leave it and combine with the iron. If a piece of copper be put into the same solution no change will take place; but if we by any means give to this copper an increased tendency to unite

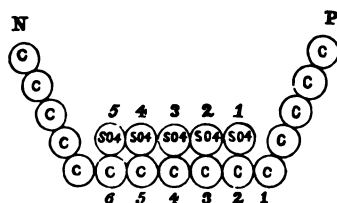


Fig. 61.

with the acid, it will attract the acid from the copper in solution by virtue of this increased affinity. Suppose two wires coming from a battery forming a chain of particles or atoms, and placed in a sulphate of copper solution, as in Fig. 61, the double row representing the compound atoms of sulphate of copper forming the electrolyte; CC the copper or positive element, and SO_4 the sulphuric acid or negative element of the solution. The two single rows CC, &c., at each end of the double row, represent the wire or solid conductors of the electricity, from the battery to the decomposition cell: the last particle of the single rows, PN, nearest the double row may be viewed as the electrodes. The sulphuric acid SO_4 , and the copper C, in solution, are held together by their affinity for each other.

Now let it be supposed that an equivalent of electricity leaves the positive terminal of the battery P, and passes along the solid particles of the conductor, that particle upon which the electricity is must be for the time in a higher state of excitement than the other particles. When the electric current comes to the last particle of the solid chain P, which is in contact with the electrolyte, its increased excitement causes it to attract and combine with the acid particle SO_4 nearest it; the electricity being dynamic, passes to the first basic particle C1, giving it an exalted excitement, which causes it to unite with the acid particle SO_4 1, the electric force passing to C2, which becomes excited

in turn, and takes the particle SO_4^{2-} ; and so on through the chain till the last particle C6, which, having no further acid to combine with, is thus left adhering to the solid chain of particles or electrode forming the deposit, and the electricity passes along the solid conductor or electrode to the battery N.

By this we observe that every equivalent of decomposition will draw an equivalent of acid to the positive electrode, without taking the metallic element to the other or opposite electrode. Whether this be the true definition of the manner in which electrolytes are decomposed by dynamic electricity, we do not affirm; but it is our opinion, and it agrees exactly with the results that take place in all solutions undergoing decomposition by a current of electricity, and also in the battery between the zinc and copper.



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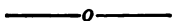
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